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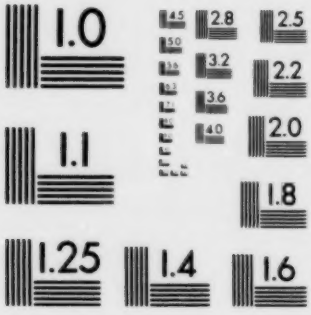

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EXPERIMENTAL EVALUATION OF CATALYST DEACTIVATION CAUSED BY ASPHALTENE ADSORPTION

Final Report

By

A.L. Court
Project Manager
NewGrade Energy Inc.

and

D.W. Soveran and C. Jackson
Saskatchewan Research Council

Work on this project was conducted under the auspices of the Canada Centre for Mineral and Energy Technology, Energy, Mines and Resources Canada

DSS File No. 07SQ.23440-5-9135
DSS Contract Serial No. 0SQ85-00308
CANMET Scientific Authority M.V.C. Sekhar

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SUMMARY

The project objective was to determine the contributing factors of the catalyst deactivation mechanisms of typical hydroprocessing catalysts. It is suspected that the asphaltene component of heavy oil feedstocks plays a major role in reducing catalyst activity. There has been limited investigation of the effect of asphaltene molecules on catalyst activity. The project was designed to determine the significance of asphaltene adsorption on catalyst activity.

Fresh catalysts (two) were impregnated with asphaltene material derived from Athabasca bitumen using a variety of techniques. Different combinations of temperature, pressure, asphaltene concentration and type of solvent were used in the impregnation techniques. The catalyst's activity was measured in a bench-scale hydroprocessing unit using a blend of pure components for a feedstock. The effect of the impregnation techniques was evaluated by determining the amount of unconverted material in the liquid products and by measuring sulphur conversion. Two catalysts from heavy oil hydrocracking experiments were also evaluated for activity.

The activity experiments did yield some important results on adequate presulphiding techniques and the effect of presulphiding. The initial experiments indicated that the catalyst was not completely presulphided. A technique obtained from the literature had been used. After modifying the presulphiding procedure, more consistent results were obtained. It was also established that during presulphiding the majority of the asphaltene material was removed from the catalyst.

Analyzing the liquid product for unconverted materials proved difficult and gave limited indication of catalyst activity. A limited number of nitrogen analyses were performed to measure denitrogenation activity. They provided a superior indication of denitrogenation activity. The sulphur conversion was calculated from the amount of H_2S in the gas product.

Two catalysts, deactivated by hydrocracking heavy oil residues, were also measured for residual activity. They were tested to determine if the asphaltene impregnations deactivated the catalysts in a similar manner. At typical hydrotreating conditions the tests indicated these catalysts retained much to their activity and it was only at very low severity conditions that their activity proved to be significantly less than the fresh catalysts. This indicates that the model compound feedstock may not be appropriate for activity measurements because it was readily converted by low activity catalysts.

The results provided very limited indication of the effect of asphaltenes on catalyst activity, but the work was valuable for the presulphiding data and the suitability of model compound feedstocks. The results also lead to several suggestions for future approaches when studying catalyst deactivation mechanisms.

Sommaire

L'objectif du projet était de déterminer quels étaient les facteurs contribuant aux mécanismes de désactivation des catalyseurs dans les catalyseurs types d'hydrotraitement . On suspecte que le composant asphaltène des charges d'alimentation d'huile lourde joue un rôle primordial dans la réduction de l'activité des catalyseurs. L'effet des molécules d'asphaltène sur l'activité du catalyseur a été peu étudié. Le projet était destiné à déterminer les conséquences de l'adsorption de l'asphaltène sur l'activité des catalyseurs.

Deux catalyseurs neufs ont été imprégnés d'asphaltène dérivé des bitumes d'Athabasca selon une variété de techniques d'imprégnation faisant jouer des combinaisons différentes de température, de pression, de concentration en asphaltène et de type de solvant. Nous avons mesuré l'activité du catalyseur dans une unité d'hydrotraitement portative en utilisant un mélange de composants purs pour chaque charge d'alimentation. Nous avons évalué l'effet des techniques d'imprégnation en déterminant la quantité de matériau non transformé dans les dérivés liquides et en mesurant le niveau de transformation du soufre. Nous avons également évalué l'activité de deux catalyseurs utilisés dans des expériences d'hydrocraquage d'huile lourde.

Les expériences de mesure de l'activité ont donné des résultats importants en ce qui concerne les techniques adéquates de présulfuration et l'effet de cette présulfuration. Les expériences initiales ont indiqué que le catalyseur n'avait pas été complètement présulfuré. Nous avions utilisé une technique suggérée dans les divers articles et journaux consultés lors de l'étude préliminaire. Après modification de la procédure de présulfuration, nous avons pu obtenir des résultats plus cohérents, et nous avons également pu établir qu'au cours de la phase de présulfuration, la plus grande partie de l'asphaltène était éliminée du catalyseur.

L'analyse des dérivés liquides pour y trouver des matériaux non transformés s'est révélée difficile, et n'a donné qu'une indication limitée de l'activité des catalyseurs. Nous avons procédé à un nombre limité de mesures de l'azote pour vérifier l'activité de désaturation en azote, et ces analyses ont fourni une indication excellente de cette activité. Nous avons calculé le niveau de transformation du soufre en mesurant la quantité de H_2S dans le dérivé gazeux.

Nous avons également mesuré l'activité résiduelle de deux catalyseurs qui avaient été désactivés lors d'expériences d'hydrocraquage de résidus d'huile lourde. Ces catalyseurs ont été testés pour déterminer si plusieurs imprégnations d'asphaltène contribuaient à les désactiver de la même manière. En condition type d'hydrotraitement, les tests ont indiqué que les catalyseurs conservaient beaucoup de leur activité, et que c'est seulement dans des conditions extrêmement rigoureuses que leur activité était réduite de manière significative par rapport à celle de catalyseurs neufs. Ceci semble indiquer que la charge d'alimentation modèle de composés purs peut ne pas être appropriée pour mesurer l'activité, en raison de sa transformation facile par des catalyseurs de faible activité.

Les résultats ont fourni une indication limitée de l'effet des asphaltènes sur l'activité des catalyseurs, mais l'étude a donné des résultats intéressants sur la présulfuration et la pertinence des charges d'alimentation modèles de composés purs. Les résultats obtenus ont également suggéré plusieurs approches futures pour l'étude des mécanismes de désactivation des catalyseurs.

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I. INTRODUCTION

The mechanism of catalyst deactivation during heavy oil upgrading is not fully understood even though several catalytic hydrocracking processes are being marketed. This is an important research problem because the economics of catalytic hydrocracking processes will depend on the activity life of the catalyst. Unfortunately catalyst deactivation is rapid for heavy oil and bitumen, especially at high conversion. Explanation of the deactivation is difficult because of the complex nature of the asphaltene molecules which poison the catalysts. In addition, during the upgrading of heavy oils and bitumens several parallel reactions (such as hydrogenation, hydrocracking, desulphurization, denitrogenation, demetallization, deoxygenation and dehydrogenation) occur because of the presence of complex hydrocarbons. Undoubtedly, research into understanding the mechanisms of poisoning and coke deposition and the resulting effect on various upgrading reactions will be extremely helpful in the long term in selecting catalysts and in developing catalysts.

There has been a limited amount of research on catalyst deactivation mechanisms. One other group[1] studied the effect of asphaltenes on catalyst activity. This project extends the scope of the previous study so that a better understanding can be obtained.

Most commercial catalysts can hydroprocess feedstocks with no asphaltene fraction for approximately one year before needing regeneration, but once asphaltenes are part of the feedstock catalyst life is dramatically reduced. It is apparent that asphaltenes are a key component of catalyst deactivation.

Asphaltene molecules are large, highly condensed aromatic structures that have a high molecular weight and contain significant contaminants (nitrogen, sulphur, oxygen, trace metals such as nickel, vanadium and iron).

It is generally agreed that the condensed aromatic components contribute coke formation on the catalyst surface. Trace metals from the asphaltenes are also deposited on the catalyst's surface. Both of these contribute to the deactivation because they block the active sites on the catalyst.

The project plan was to adsorb the asphaltene material onto the catalyst and determine how each adsorption technique contributed to catalyst deactivation. Catalyst impregnation methods used different combinations of asphaltene concentration, solvent, pressure and temperature. The activity was then measured by processing a feedstock mixture of pure components under typical hydroprocessing conditions. The activities of catalysts that had been used to hydroprocess heavy oil and bitumen feedstocks were also tested.

2. EXPERIMENTAL

There are several components to the experimental program. A literature survey was undertaken to determine if any similar research had been performed in this area, as well as to obtain suitable catalyst impregnation conditions, appropriate model compounds and associated hydroprocessing conditions. Catalysts were selected based on the experience of the subcontractor and the Scientific Authority. A technique for extracting sufficient quantities of asphaltene material was developed. A two-litre batch autoclave was modified for the impregnation experiments. A manually operated continuous hydroprocessing unit was designed and built for the catalyst activity determinations. A gas chromatograph (GC) method was also developed to analyze the liquid products.

2.1 Literature Survey

The literature survey was performed to determine typical model compounds, operating conditions, presulphiding procedures and asphaltene impregnation techniques. The assembled articles provided a wide array of alternatives for this project.

Most researchers used less than three model compounds for study. For example, Faus et al[1] used a mixture of cyclohexane, cyclohexene and thiophene. Five reactions were monitored in their study: hydrogenation of cyclohexene to cyclohexane; formation of benzene; reduction of thiophene; and isomerization reactions, which resulted in the formation of methlycyclopentane and methylcyclopentene. Other model compounds frequently used include dibenzothiophene, naphthalene, cumene, quinoline, toluene, and isoctene.

Most model compound work ignores the interaction between chemical compounds. This is important because catalysts often perform significantly different with model compounds in comparison to petroleum feedstocks. The

approach taken in this work was to select a number of typical model compounds and use a mixture similar in makeup to heavy oil feedstocks. The first mixture included twelve components. The resulting product proved to be too difficult to analyse, and the feed mixture was reduced to seven compounds.

The hydrotreating conditions employed spanned a broad range. Reactor temperatures ranged from 220-450°C and the hydrogen partial pressures were from atmospheric to 12 MPa. The liquid hourly space velocity ranged from 0.5 to 10 hr^{-1}. One of the more valuable references, Chu and Wang,[20] selected a range that covered conditions typically utilized in commercial hydrotreaters. Vrinat,[29] in his review work in hydrodesulphurization, observed that it is difficult to compare the work of various researchers because the selected conditions are not within normal commercial ranges. Operating parameters for the activity measurements were selected to be comparable to commercial practice. The conditions were subsequently modified after it was concluded they were too severe for the model compound feedstock.

The presulphiding procedures outlined in the literature were generally quite similar. Most used hydrogen sulphide as the sulphur source while a limited number used dimethyl disulphide or carbon disulphide. Typical reactor conditions were 300-400°C (depending on the sulphur source) and atmospheric pressure. A typical procedure was used by Sapre and Gates[22] where H_2S in H_2 was the sulphur source, reactor conditions were 400 °C and atmospheric pressure, maintained for two hours. They assumed that since they provided more than twice the required amount of sulphur the catalyst would be adequately presulphided. A similar procedure was used initially in the activity experiments. It was readily apparent that the procedure did not adequately presulphide the catalyst. After some experimentation, it was determined that presulphiding under pressure (at least 3.5 MPa) was necessary to fully activate the catalyst.

Faus, Grange and Delmon[1] provided the only reference to asphaltene impregnation of a catalyst. Three methods were used by Faus et al. In the first, presulphided catalyst was impregnated with asphaltene in the reactor by flowing an asphaltene in xylene solution over the catalyst. At the completion of the impregnation procedure the remaining xylene would be evaporated off. They found that the greatest catalyst deactivation occurred with high temperature and high pressure impregnation. Repeated impregnations were done by mixing the catalyst with an asphaltene-xylene mixture and then evaporating the xylene off. Physical mixing the catalyst with asphaltene material (no solvent) was also tried. It caused more deactivation than a repeated impregnation method.

A different impregnation technique was developed in this work. Methods similar to the first technique used by Faus were tried. All the impregnations were done in batch reactor under different combinations of temperature, pressure, asphaltene concentration and solvent. The objective was to have the asphaltene material distributed equally over the surface of the catalyst rather than just coating the external surface of the pellets.

Numerous variations of asphaltene extraction methods were found. Speight et al[14] provide an informative discussion of such factors as solvent type, solvent to oil ratio, use of benzene as a thinner, contact times, and the use of heat to cause coagulation. A method similar to a commonly used analytical technique for determining asphaltene content was adapted for large sample volumes.

A bibliography is included in Section 5.

2.2 Catalyst Impregnation

A series of impregnation conditions were developed in conjunction with the Scientific Authority. One of the two fresh catalysts was to be impregnated under all conditions. The catalyst's activity was then measured and a selection of the most effective conditions made. The second fresh

catalyst was then impregnated at the selected conditions and the activity determined.

All impregnations were performed in a modified batch autoclave that could be controlled at any combination of pressure and temperature up to 20.7 MPa and 500°C. An inert gas (argon) was used to blanket the solvent, asphaltene and catalyst mixture. The autoclave's stirrer had to be lengthened so that it was fully immersed in the mixture. A glass liner was also used to simplify the retrieval of the catalyst.

The selected series of conditions was as follows:

Method	Temperature	Pressure	Solvent	Asphaltene/ Solvent Ratio
1	22°C	atm	dekalin	1:10
2	100	atm	dekalin	1:10
3	200	atm	dekalin	1:10
4	22	atm	dekalin	2:10
5	22	atm	dekalin	3:10
6	22	atm	tetralin	1:10
7	22	atm	cyclohexane	1:10
8	22	atm	toluene	1:10
9	200	4.2 MPa	dekalin	1:10
10	200	6.2 MPa	dekalin	1:10
11	300	4.5 MPa	dekalin	1:10
12	300	8.3 MPa	dekalin	1:10

Each impregnation follows the same basic procedure:

1. Place 30 g of catalyst in the autoclave glass liner.
2. Add the appropriate amount of asphaltene to the catalyst.
3. Add the desired solvent and quantity as required by the solvent/catalyst ratio.
4. Shake and rotate liner to mix the catalyst, solvent and asphaltenes.
5. Place liner in the autoclave and seal.
6. Purge the autoclave with argon and establish the desired conditions.

7. Stir the mixture at the conditions for 4 h with the stirrer set at 100 rpm.
8. Cool and depressurize the autoclave if necessary and remove the liner and mixture. If cool down is necessary, cold water is put through an internal cooling coil to condense any vaporized solvent into the liner.
9. Wash the catalyst with pentane until clear.
10. Extract the catalyst with pentane in a soxhlet for 1.5 h.
11. Dry catalyst at room temperature under vacuum for 1 h.
12. Place catalyst in an airtight container and flush with argon. Store the catalyst in a freezer.

2.3 Asphaltene Extraction

The method used to extract the asphaltene material was basically the analytical technique used for determining the asphaltene content in an oil. The solvent used was pentane. Approximately 200 g of asphaltenes were required for the impregnations so the technique had to be scaled up. Six extractions, yielding approximately 30-40 g of asphaltenes each, were performed.

The method is as follows:

1. Mix 250 mL of Athabasca bitumen and 60 mL of toluene. This reduces the viscosity of the bitumen and aids dispersion in the pentane.
2. Add the mixture to 4 L of agitated pentane.
3. Stir the mixture for 2 h at room temperature.
4. Let stand overnight to allow the precipitate to settle out. Total contact time with the pentane, including mixing, is 18 h.
5. Decant about three quarters of the pentane. Filter the remainder through a thimble.
6. Extract the precipitate in a soxhlet with pentane until the wash is colorless (about 5-6 h).
7. Dry the precipitate at 35°C, 27 in. Hg for 3 h.

8. Store the precipitate under nitrogen at -17°C.

2.4 Catalyst Selection

Two fresh and two deactivated catalysts were selected for activity measurements. American Cyanamid HDS-20 was selected by SRC because it had been used by them in a number of heavy oil hydroprocessing experiments. CANMET supplied a sample of a Harshaw cobalt-molybdenum catalyst as the other fresh catalyst. Activities of fresh and impregnated catalysts were determined. SRC also provided a deactivated sample of HDS-20. CANMET provided a fresh and deactivated sample of F145 for testing.

2.5 Catalyst Presulphiding

Presulphiding methods were also investigated in the literature. The method commonly practiced at SRC uses a virgin gas oil spiked with carbon disulphide (CS_2) as a feed. The temperature is increased in steps from 100°C to 320°C over a 16 h period. Although effective it was clearly too time-consuming for the number of short runs to be performed in this project. It would also contaminate the unit with another liquid feedstock, which would take at least 24 hours of operation to clear satisfactorily.

The method selected used a 10% H_2S, 90% H_2 mixture at atmospheric pressure, 400°C for 4 h. The quantity of sulphur was approximately six times the required amount. This method proved inadequate because during the first activity experiments it was apparent that the catalyst was not completely presulphided. The H_2S content in the product gas took approximately 4 h to stabilize whereas it was expected to stabilize within an hour. To complete presulphiding, an extra activity experiment was carried out at 400°C and 6.9 MPa for 4 h using the liquid feed as the sulphur source. This method yielded better results, but it added another day of operation to each series.

Presulphiding with the same gas mixture at the same temperature and a pressure of 3.4 MPa was tried. This procedure was more successful in providing adequately presulphided catalyst.

2.6 Feedstock Selection

The literature was surveyed for suitable pure components for the activity experiments. The intent was to select a mixture of components that would test the activity of the catalyst and be similar in nature to a heavy oil feedstock (without the asphaltene content). The initial selection included:

1. Cyclohexene
2. Cyclohexane
3. Thiophene
4. 1-Isoctene
5. 1-Hexene
6. Pyridine
7. Pyrrole
8. Quinoline
9. Benzothiophene
10. Aniline
11. Naphthalene
12. Cumene

The feedstock was a blend of the pure compounds, which approximated the composition of Lloydminster crude. Total sulphur was limited to about 4 wt % and nitrogen to about 0.4 wt %. The precise makeup was as follows:

Lloydminster Crude	Model Compound	Wt % in Mixture
32.9% saturates	cyclohexane	19.0
	cyclohexene	10.0
	1-isoctene	2.0
	1-hexene	2.0
12.5% mononuclear aromatics	toluene	30.7
	cumene	12.5
7.0% dinuclear aromatics	naphthalene	7.0
11.4% polynuclear aromatics	none (toluene)	

11.9% Polar Compounds	thiophene	5.0 (1.91% S)
	thianaphthene	9.0 (2.15% S)
	pyrrole	0.6 (0.13% N)
4.9% Basic Compounds	pyridine	0.6 (0.11% N)
	quinoline	0.9 (0.10% N)
	aniline	0.7 (0.11% N)
19.3% Asphaltenes	none (toluene)	

The complex mixture was utilized for three activity measurements. The resulting liquid product contained many derivatives of the feed components. This made the analysis almost impossible. A simpler feedstock with the following components was selected for subsequent experiments.

Component	Wt %
Cyclohexane	26.0
Cyclohexene	13.4
Isoctene	10.0
Toluene	30.0
Naphthalene	7.0
Thiophene	10.0 (3.82% S)
Quinoline	3.6 (0.39% N)

2.7 Liquid and Gas Product Analysis

The liquid product from the activity measurements was to be analyzed for unconverted components using a gas chromatograph (GC). Both model compound mixtures were used to develop a suitable GC technique. A long capillary column was necessary to provide adequate separation of the compounds. Columns SRC had on hand were tried with limited success, but the type and length of the column necessary to perform the analysis were determined. A 50-m x 0.53-mm ID capillary column with 3.0 μ film of methyl silicone was purchased and installed in the GC. The GC was calibrated with the feed mixtures. The column was used in a Varian model 6000 GC.

The gas product was sampled using a gas tight syringe. The sample was then immediately injected into a Carle GC for analysis. The Carle is an

isothermal mode GC capable of providing very reliable analysis of C_1-C_5 hydrocarbons including olefins and isomers as well as H_2, CO, CO_2, N_2 and O_2.

2.8 Hydroprocessing Conditions for Activity Measurements

It was anticipated that relatively severe conditions would be necessary to convert a meaningful amount of many of the feed components. The conditions were selected based on information found in the literature and in-house hydroprocessing experience. The experimental design[30] was based on two factors, the reactor temperature and the hydrogen partial pressure. The temperature limits were 300°C and 400°C while the pressure limits were 3.4 MPa and 6.9 MPa. The liquid hourly space velocity was set at 1.75 hr^{-1} and the hydrogen flow rate set at 900 cm^3 H_2/cm^3 liquid feed.

The resulting series for each catalyst would be:

Run No.	Temperature (°C)	Pressure (MPa)
1	350	5.2
2	300	3.4
3	400	3.4
4	400	6.9
5	300	6.9
6	350	5.2

As mentioned in Section 2.5, inadequate presulphiding caused an increase in the number of runs to seven when it was decided to complete presulphiding with the liquid feed.

Upon completion of several activity experiments and the analysis of the liquid products, it appeared that complete conversion of many of the feed components was occurring. The series was modified with different temperature and pressure limits.

The revised series is:

Run No.	Temperature (°C)	Pressure (MPa)
1	350	5.2
2	300	3.4
3	250	5.2
4	350	2.7
5	250	2.7
6	300	3.4

All remaining catalyst activity experiments were performed at the revised conditions.

2.9 Construction and Commissioning of an Experimental System

A new 30-mL reactor system was constructed for this project (although it was not funded by this contract). Figure 1 is a schematic of the unit. A manually-controlled system, it is basically a liquid feed pump, an upflow fixed bed reactor and a gas liquid separator. A back pressure regulator (BPR) controls the system pressure. Liquid is drained from the separator manually at regular intervals. The reactor has three temperature controlled zones. The hydrogen flow is controlled with an electronic mass flow controller. The gas product was scrubbed in a caustic (sodium hydroxide) solution to remove H_2S and then measured with a wet test meter. The liquid feed rate was monitored by weighing the feed vessel on a constant basis.

Two different reactor designs were used over the course of the project. The first reactor had three radially inserted thermocouples mounted on thick stainless-steel rings. The rings acted like large heat sinks and caused significant heat loss and temperature control problems. After a few experiments, this reactor was replaced with a simple tube reactor with an an axially inserted multipoint thermocouple and superior operation was achieved. Most of the activity experiments were performed with the simple reactor.

During the course of the experiments a number of modifications were made to enhance the operation of the unit. A liquid knockout pot was added on the gas product lines because the gas liquid separator was heated

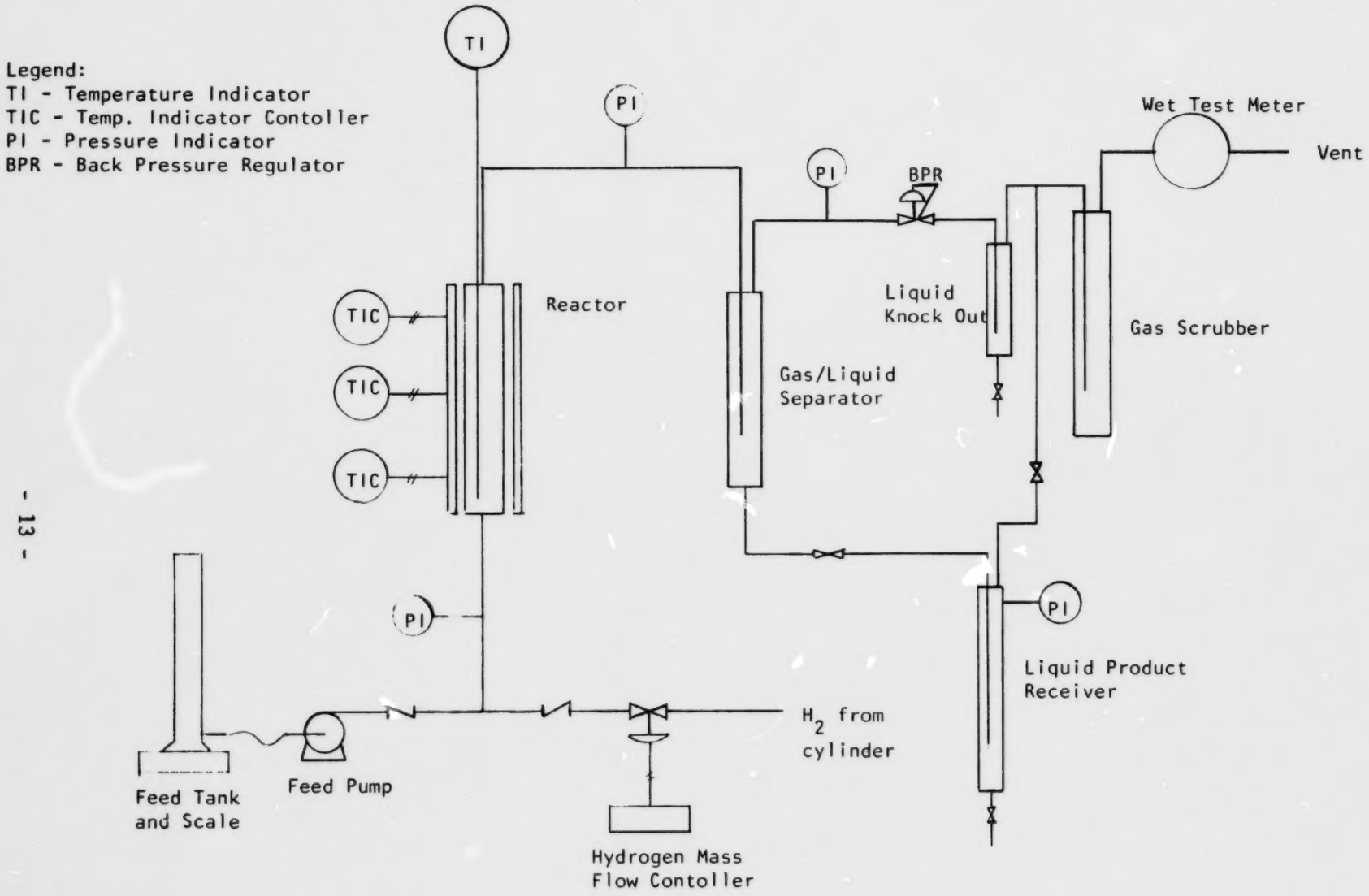


Figure 1. Schematic of 30-ml Hydroprocessing Unit

slightly causing some liquid carryover. The BPR was heated as well because of the liquid carryover problem. Most of the liquid product lines were heated after an accumulation of naphthalene and other crystals was discovered.

The unit had several data points that were logged by a computerized data acquisition system. Six thermocouples and three pressure transducers were monitored with the system.

2.10 Calculation of Hydrogen Consumption and Sulphur Conversion

The calculated results have a significant amount of errors primarily because of the short length of each experiment (3-4 hours). Both calculations rely on an average gas analysis, that is an average of two or three analyses. The gas composition does not achieve equilibrium until about 1.5 hours into the experiment. If the experiments were longer, the initial period to reach equilibrium could be discontinued. It was necessary to perform two experiments in a nine hour day, however, as the initial period had to be included so that sufficient product could be gathered for each experiment. Because all experiments and subsequent calculations were performed in a like manner, it is reasonable to compare the consumption and conversion data of the different activity measurements.

2.10.1 Hydrogen Consumption

The hydrogen consumption was calculated from a hydrogen balance performed for each experiment. Hydrogen is fed to the unit through an accurate mass flow controller. The product gas is analyzed prior to scrubbing in a sodium hydroxide (NaOH) solution to remove hydrogen sulphide (H_2S). The product gas volume is measured in a wet test meter prior to venting. A sample calculation is given below.

Experiment No. HDS20FB
Catalyst: Fresh HDS-20
Reaction Conditions: 350°C, 5.2 MPa
Product Gas Volume: 123 L (H_2S free)
Average Product Gas Temperature: 22.8°C
Average Barometric Pressure: 717.8 mmHg

Total Hydrogen Feed: 142.52 L (@1 atm, 15°C)

Average Product Gas Analysis (mol %)

Hydrogen	95.337
Propane	0.010
H_2S	2.562
Iso-butane	0.039
n-Butane	1.926
Nitrogen	0.126
Total	100.000

Correct product gas to 1 atm, 15°C (H_2S free):

$$V_g = 123\ L \left(\frac{717.8\ mmHg}{760\ \ mmHg}\right)\left(\frac{298}{22.8+273}\right) = 117.0\ L$$

Calculate product gas volume to include H_2S:

$$117\ L \left(\frac{100}{100-2.562}\right) = 120.1\ L$$

Calculate moles of gas:

$$120.1\ L\left(\frac{1\ gmol}{23.68\ L}\right) = 5.072\ gmol$$

Moles of hydrogen fed:

$$142.52\ L\left(\frac{1\ gmol}{23.68\ L}\right) = 6.018\ gmol$$

Moles of hydrogen in product gas:

$$(0.95337)\ (5.072\ gmol) = 4.836\ gmol$$

Hydrogen consumed:

$$6.018 - 4.836 = 1.182 \text{ gmol}$$

Hydrogen consumption per gram of liquid feed:

$$\frac{1.182 \text{ gmol } H_2}{137.3 \text{ g liquid}} = \frac{0.0086 \text{ gmol } H_2}{\text{g liquid feed}}$$

2.10.2 Sulphur Conversion

Sulphur conversion was calculated from the amount of H_2S in the product gas. Sulphur analysis of the liquid product was not performed. The remaining thiophene content in the liquid was not a reliable measure of the liquid's sulphur content because it was suspected that thiophene was being hydrogenated but not completely converted to H_2S and butane.

Using the same experiment, HDS200FB, an example calculation follows.

Sulphur in the liquid feed:

(wt fraction of sulphur in liquid feed) x (total feed)

$$(0.0382) \quad (137.3 \text{ g}) = 5.24 \text{ g}$$

Moles of H_2S in product gas:

$$(0.02562) \quad (5.072 \text{ gmol}) = 0.130 \text{ gmol}$$

Sulphur in product gas:

$$(0.130 \text{ gmol}) \left(\frac{32.06 \text{ g}}{}\right) = 4.17 \text{ g}$$

Conversion:

$$\frac{4.17 \text{ g in product gas}}{5.24 \text{ g in liquid feed}} \times 100 = 79.6 \%$$

III. RESULTS AND DISCUSSION

With the large number of activity experiments (in excess of 120), there is considerable information to sort through and present in a meaningful fashion. The results are inconclusive when trying to determine the effect of the asphaltene impregnations. The activity of the impregnated catalysts was seldom significantly less than the fresh catalyst activity. In some instances the activity was actually increased after being impregnated. The primary object of determining the effect of asphaltenes on catalyst activity was not achieved. As other significant results were obtained, the work can be viewed as an important contribution to research on catalyst testing.

The experimental data are summarized in tables provided in Appendix I. One table is given for each catalyst activity series. The information provided includes the material balance for each experimental period, hydrogen consumption, liquid and gas yields, sulphur conversion and conversion of the individual model compounds.

The data are discussed by comparing the effect of the individual impregnation techniques. Some of the conversion data are also presented graphically to simplify interpretation. A discussion of the presulphiding techniques and the suitability of the model compound feedstocks is provided under separate headings in this section.

3.1 Literature Survey

The results of the literature survey were discussed in Section 2.1. The survey provided only a single reference (Faus et al[1]) that explored the effect of asphaltene adsorption on catalyst activity. There were several shorthcomings in Faus's experimental procedure. Different impregnation techniques were tried in this work to avoid the problems of Faus's work. The result was that the catalyst and all the system internals were coated

with asphaltenes. It was hoped the procedures developed here would impregnate the catalyst uniformly over the catalyst surface (into the pores as well) not just the outer surface.

The survey was useful in providing information regarding commonly used model compounds, typical reaction conditions, and typical presulphiding procedures.

The experimental results indicate several shortcomings in common practices made by several researchers when evaluating catalytic activity. These will be discussed in the succeeding sections.

3.2 Nitrogen and Sulphur Conversion

Nitrogen conversion was to be measured by determining the quinoline content in the liquid product. It was anticipated that the quinoline would either be converted to a non-nitrogen containing compound or pass through unconverted. After several activity measurements, the analyses indicated that in almost all the liquid products there was only a small amount of quinoline remaining. However, the liquid product retained the very characteristic odour of nitrogen compounds. At that point, some further analyses were made to determine the removal of nitrogen.

The liquid products from two catalyst series, fresh catalyst and one impregnated at 300°C and 8.3 MPa, were analysed for nitrogen content. The results are given Table 1. It was unexpected that liquid products from similar reaction conditions gave similar results for both catalysts. The nitrogen levels also indicated that the quinoline had been converted to another nitrogen compound. Although no further analysis was made, it is surmised that the quinoline was easily hydrogenated to form an intermediate saturated ring compound. The compound was converted at the more severe reaction conditions (above 350°C and 6.9 MPa) and the majority of the nitrogen was removed.

A similar reaction was probably occurring with thiophene as well. The analyses also gave low thiophene levels, but product gas H_2S values indicated different degrees of thiophene conversion. The sulphur conversions were calculated based on the amount of H_2S made during the experiment.

TABLE 1 - Nitrogen Analysis of Liquid Products

Exp No.	Temp (C)	Press (MPa)	Nitrogen (ppm by wt)
HDS20FI	250	1.7	3290
HDS20FH	350	1.7	2946
HDS30FE	300	3.4	2193
HDS20FG	250	5.2	1890
HDS30FB	350	6.9	51
HDS30FA	400	6.9	25
8701LE	250	1.7	2758
8701LD	350	1.7	2677
8701LB	300	3.4	1976
8701LC	250	5.2	2422
8701LA	350	6.9	125

3.3 Effects of Impregnating the HDS-20 Catalyst

3.3.1 Effect of the Impregnation Temperature

Fresh HDS-20 was impregnated with a 9 wt % solution of asphaltenes in dekalin at 22, 100 and 200°C. The corresponding activity experiments for these impregnations were 8701A, 8701B and 8701C, respectively. The results were compared to the fresh catalyst series, HDS20F. Some of the conversion

data are presented in Figures 2, 3 and 4. The activity measurements for these catalyst were performed using the higher severity conditions.

Figure 2 compares the cyclohexene conversion of the various catalysts. The graph shows that conversion is nearly complete for all conditions. The impregnated catalysts show a slightly greater activity at the lower temperature (300°C).

Iso-octene conversion, Figure 3, is also almost complete for all conditions. Some reduction in activity can be seen for the catalyst impregnated at 20°C.

Sulphur conversion, Figure 4, shows that the fresh catalyst had lower activity in the majority of the measurements. The impregnated catalysts performed better, especially the 22°C catalyst. Sulphur conversion also increased, in almost all cases, over the experimental series possibly indicating that the catalyst's activity had not stabilized.

Conversion of the other components, toluene and naphthalene, followed similar patterns. Toluene conversion was generally very low while naphthalene conversion was typically high. Quinoline and thiophene also appeared to be completely converted but not necessarily to non-nitrogen and non-sulphur containing compounds. Cyclohexane was essentially unconverted. It was apparent that cyclohexene was converted predominantly to cyclohexane because the amount of cyclohexane would increase at the same rate of disappearance of cyclohexene.

Figure 2: CYCLOHEXENE CONVERSION

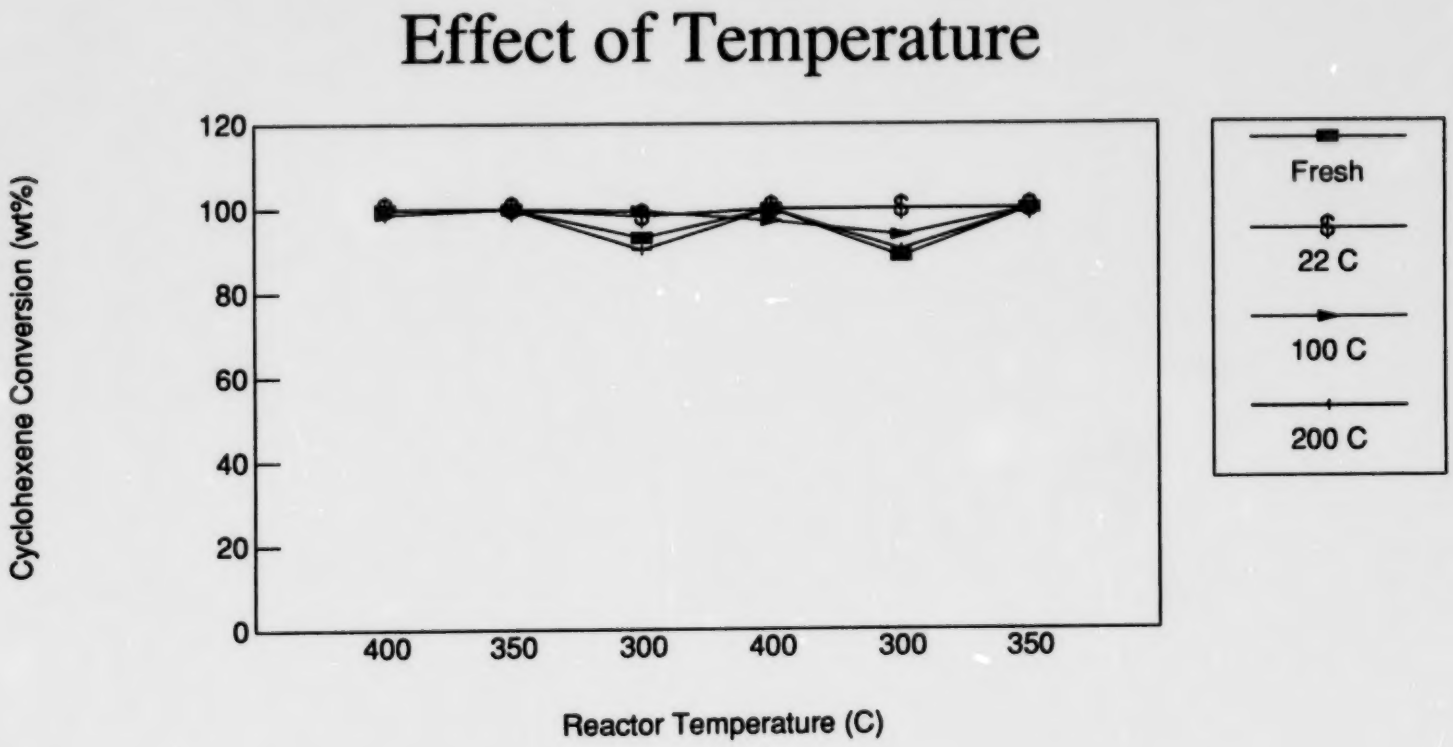


Figure 3: ISO-OCTENE CONVERSION

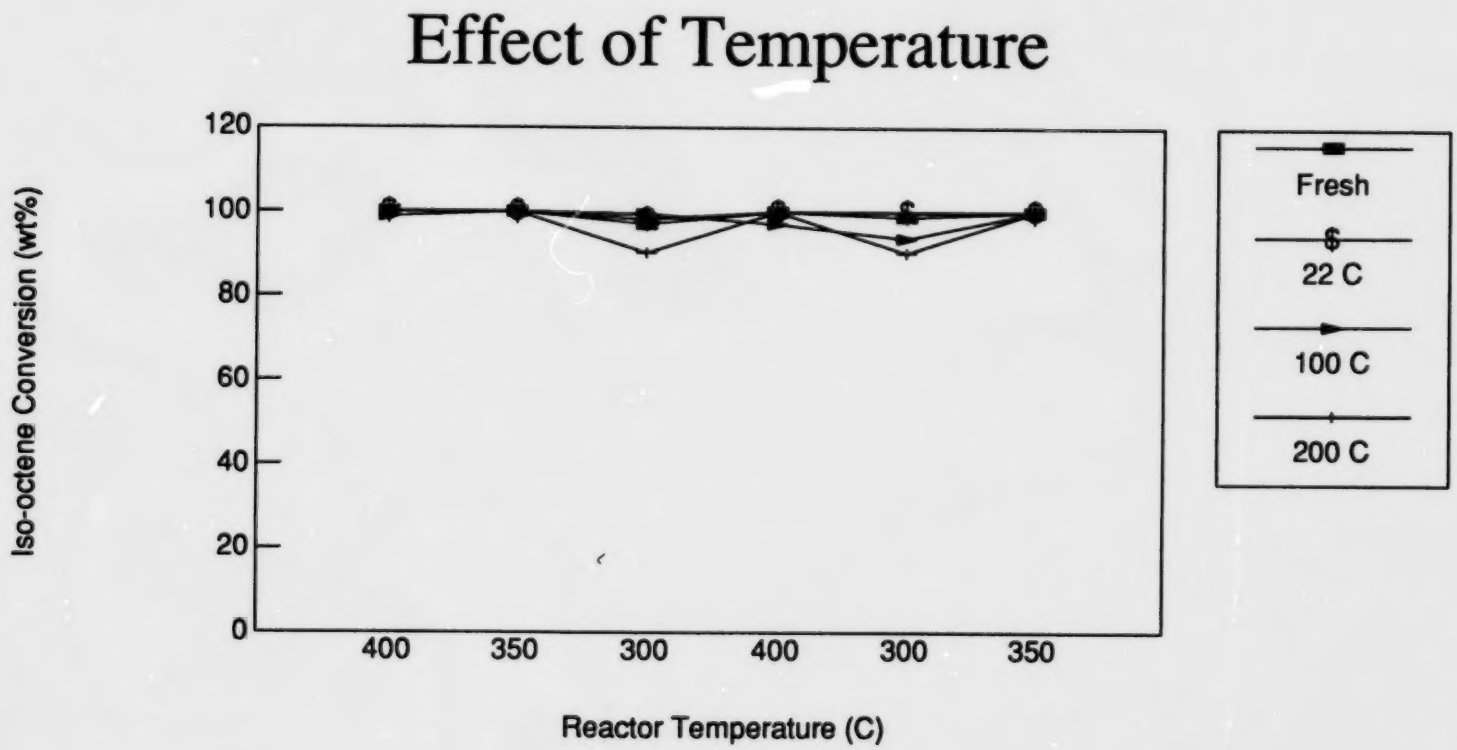
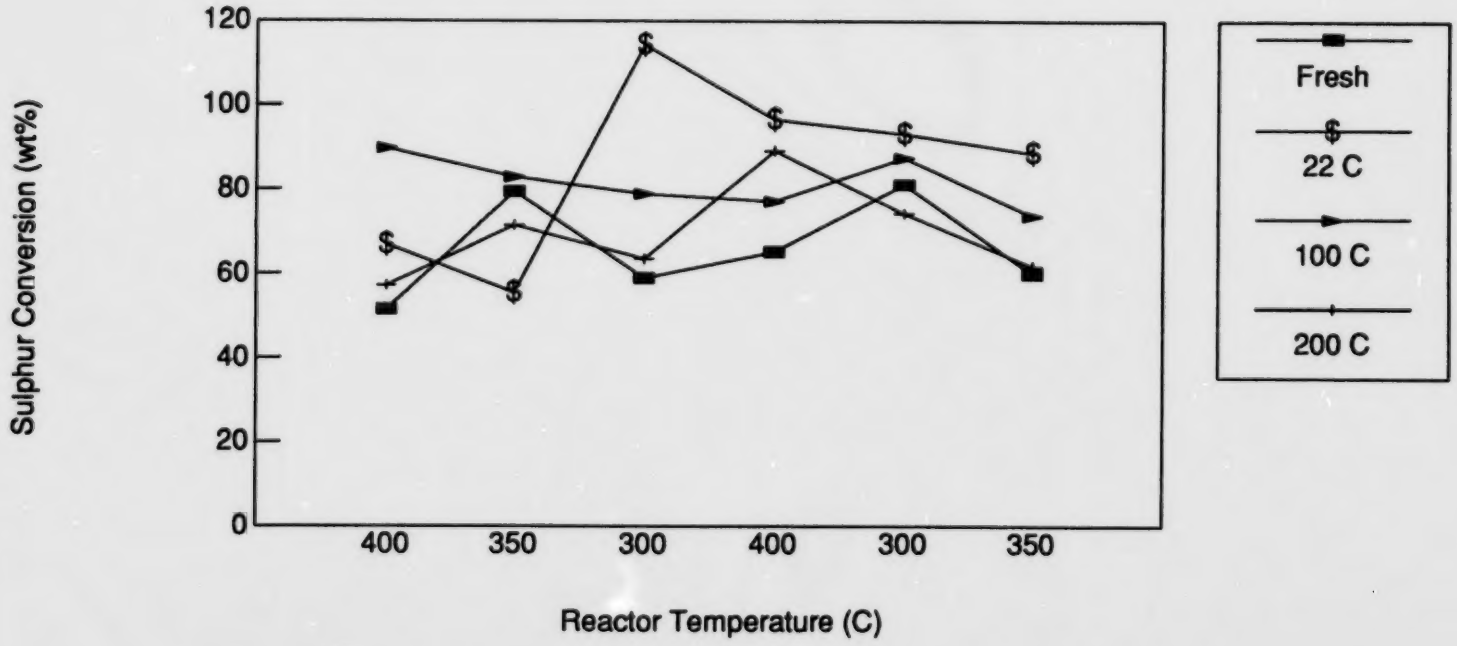


Figure 4: SULPHUR CONVERSION

Effect of Temperature



3.3.2 Effect of Asphaltene Concentration

Fresh HDS-20 was impregnated using solutions with three different asphaltene concentrations, 9, 17 and 23 wt % in dekalin. The impregnations were performed at 22°C and atmospheric pressure. The corresponding activity measurement series were 8701A, 8701D and 8701E. Figures 5, 6 and 7 compare some of the conversion data with the fresh catalyst series. After impregnating the catalyst with the two highest concentration solutions, the catalyst appeared coated with asphaltene material. The low concentration solution tended to blacken the catalyst, but its appearance was quite similar to the fresh catalyst as the porous nature of the surface was still quite evident. The activity measurements were performed at the high severity conditions.

Cyclohexene conversion, given in Figure 5, shows little effect of the impregnations. At the lowest reaction temperature the higher concentration impregnations do reduce the catalyst's activity. Figure 6 shows only a slight reduction in activity and again only at the lowest temperature.

Sulphur conversion, Figure 7, shows very little difference between the impregnated catalysts and the fresh catalyst. The low concentration catalyst shows an activity improvement at a majority of the conditions.

Conversion of the other components was similar to the temperature effect series. Naphthalene, thiophene and quinoline were almost completely converted in most cases, while toluene conversion was quite low. Cyclohexane also passed through unconverted.

3.3.3 Effect of Solvent

Fresh HDS-20 was impregnated with a 9 wt % asphaltene solution using dekalin, tetralin, cyclohexane and toluene as solvents. All the impregnations were done at 22°C and atmospheric pressure. The corresponding activity measurement series were 8701A, 8701F, 8701G and 0701H. Some of the

conversion data are compared with the fresh catalyst series in Figures 8, 9 and 10. Two of the series, 8701A and 8701F, were done at the lower set of conditions. The fresh catalyst was tested at all the different conditions.

Cyclohexene conversion, Figure 8, shows limited consistent difference between the catalysts. The catalyst impregnated using the toluene solution does show lower activity in three cases. Iso-octene conversion, Figure 9, shows even less difference between the catalysts. A different observation can be made when comparing sulphur conversion, Figure 10, where the fresh catalyst has a consistently lower activity than the impregnated catalysts. Conversion of the other components is quite similar for all the catalysts.

3.3.4 Effect of Temperature and Pressure

Fresh HDS-20 was impregnated with 9 wt % asphaltene in dekalin solution at 22°C, atmospheric pressure; 200°C, 4.1 MPa; 200°C, 6.2 MPa; 300°C, 4.2 MPa and 300°C, 8.3 MPa. The related activity series were 8701A, 8702I, 8701J, 8701K and 8701L. Figures 11, 12 and 13 compare some of the conversion data with the fresh catalyst series. Two series, 8701I and 8701L, were done at the high severity conditions.

Cyclohexene conversion was largely unaffected by the asphaltene impregnations. At the lower severity activity measurements, particularly the lower pressures, two catalysts (200°C, 4.1 MPa and 300°C, 8.3 MPa) were significantly less active than the fresh catalyst, but quite comparable at other conditions.

Iso-octene conversion was similar to the fresh catalyst pretty well throughout the series, no dramatic differences could be determined.

Figure 5: CYCLOHEXENE CONVERSION

Effect of Asphaltene Concentration

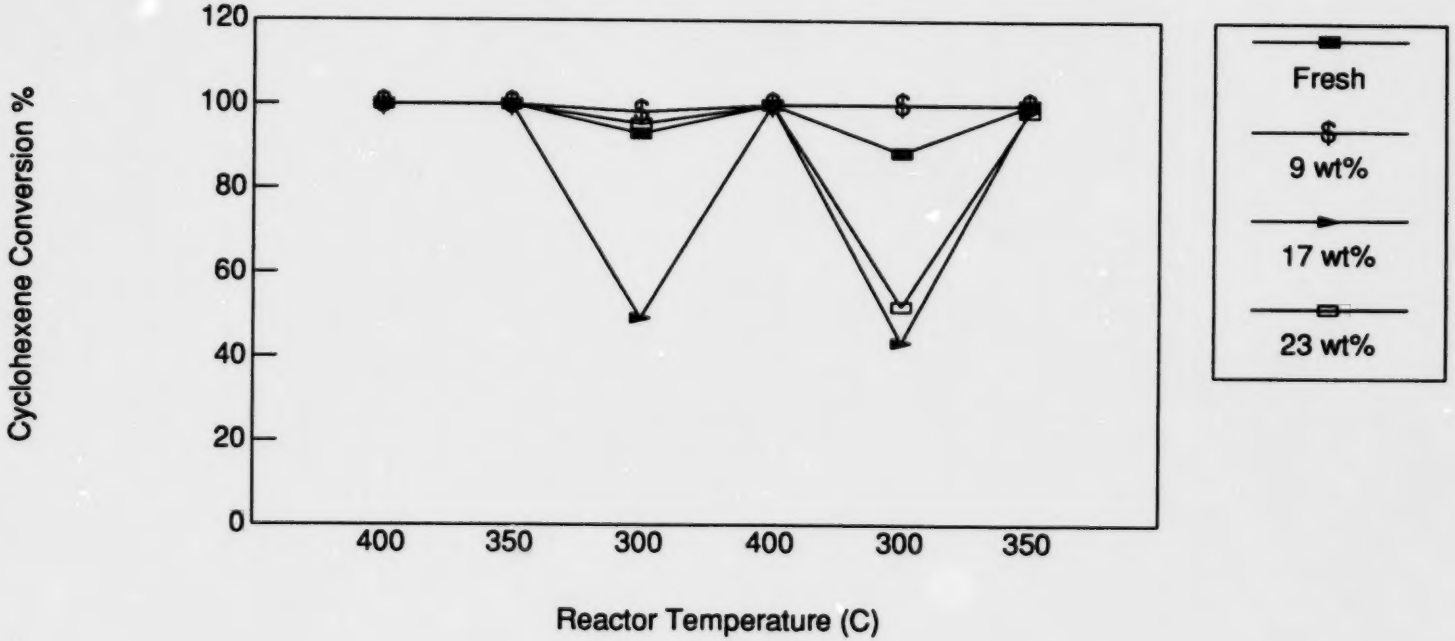


Figure 6: ISO-OCTENE CONVERSION

Effect of Asphaltene Concentration

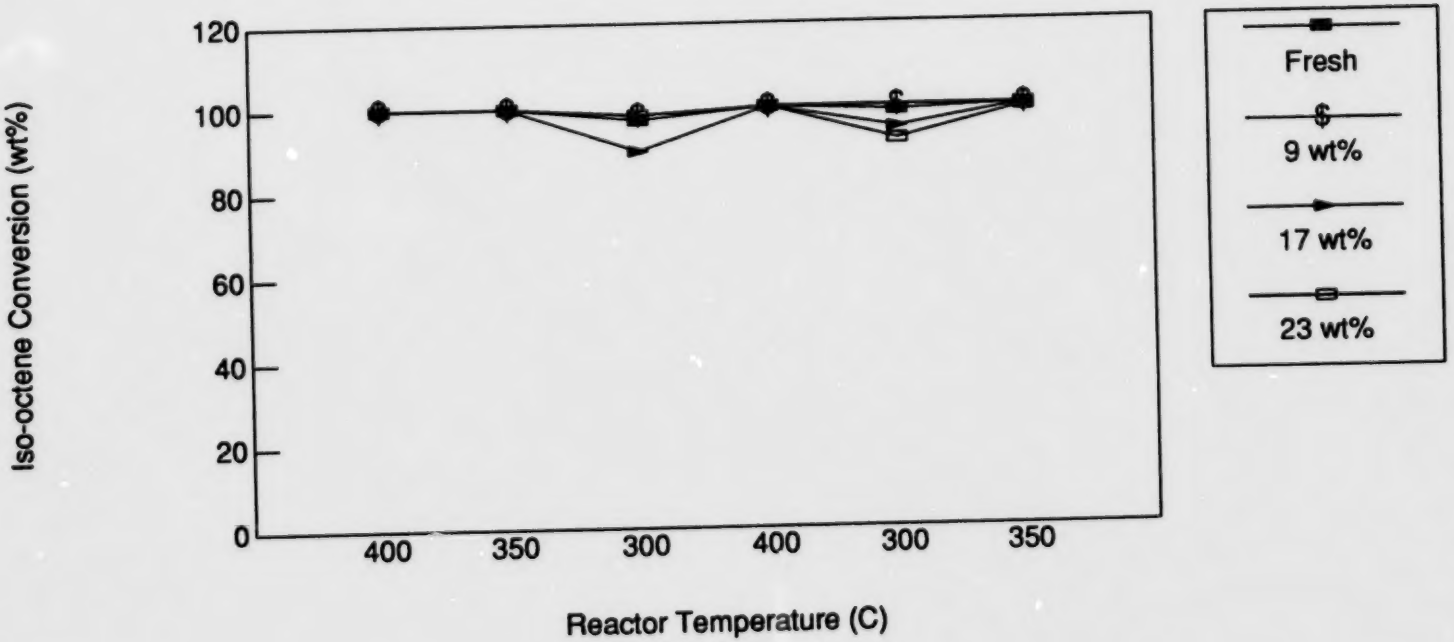


Figure 7: SULPHUR CONVERSION

Effect of Asphaltene Concentration

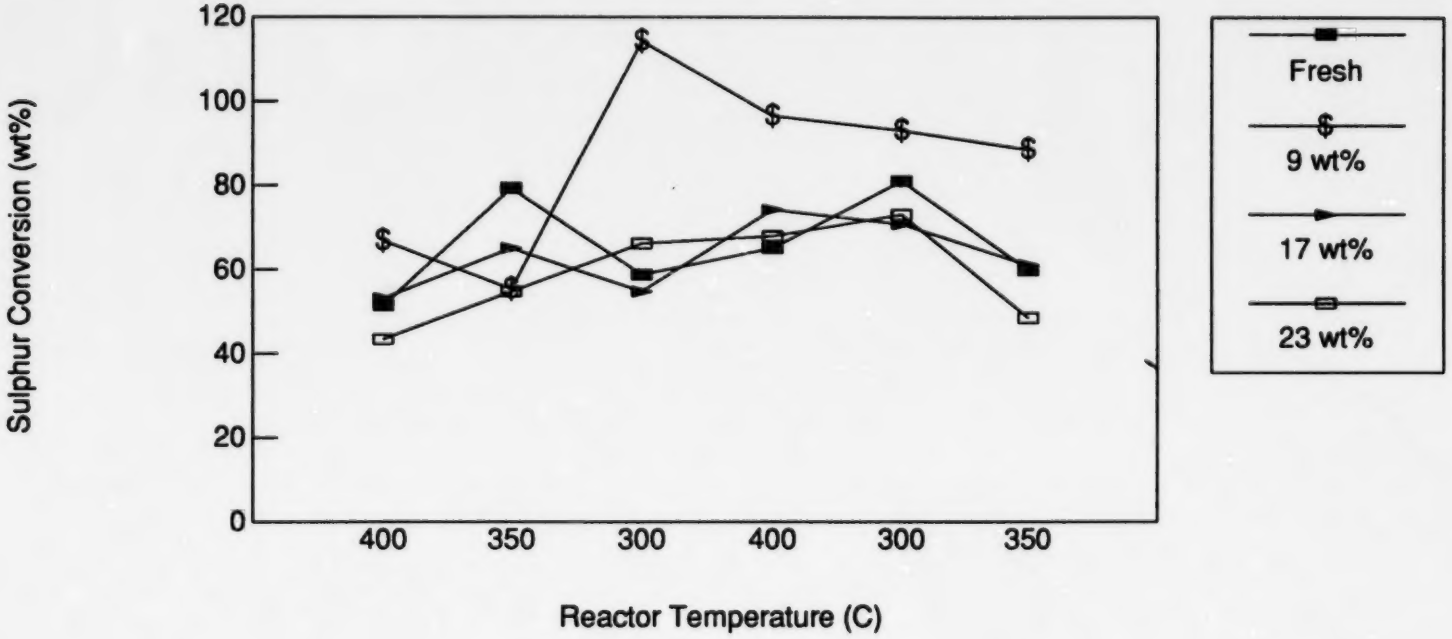


Figure 8: CYCLOHEXENE CONVERSION

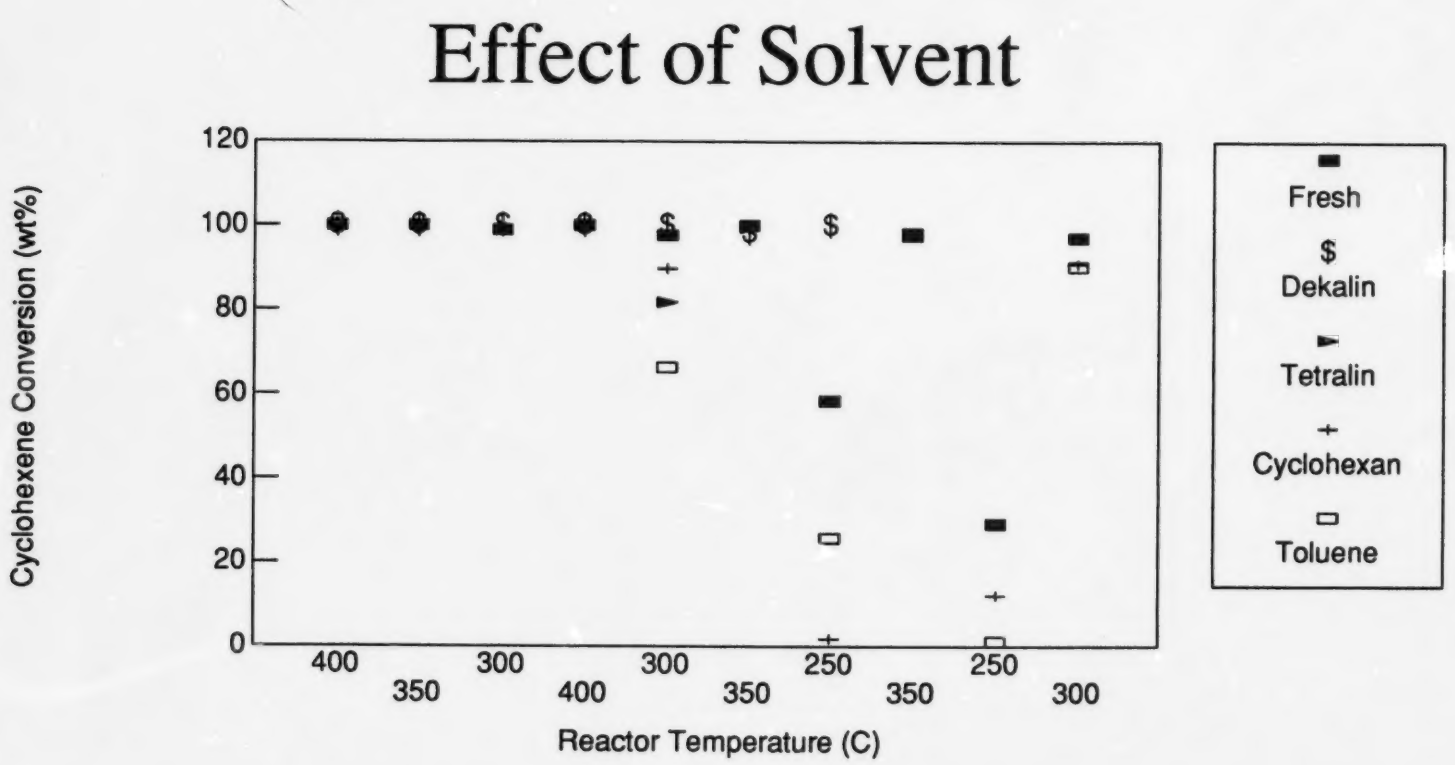


Figure 9: ISO-OCTENE CONVERSION

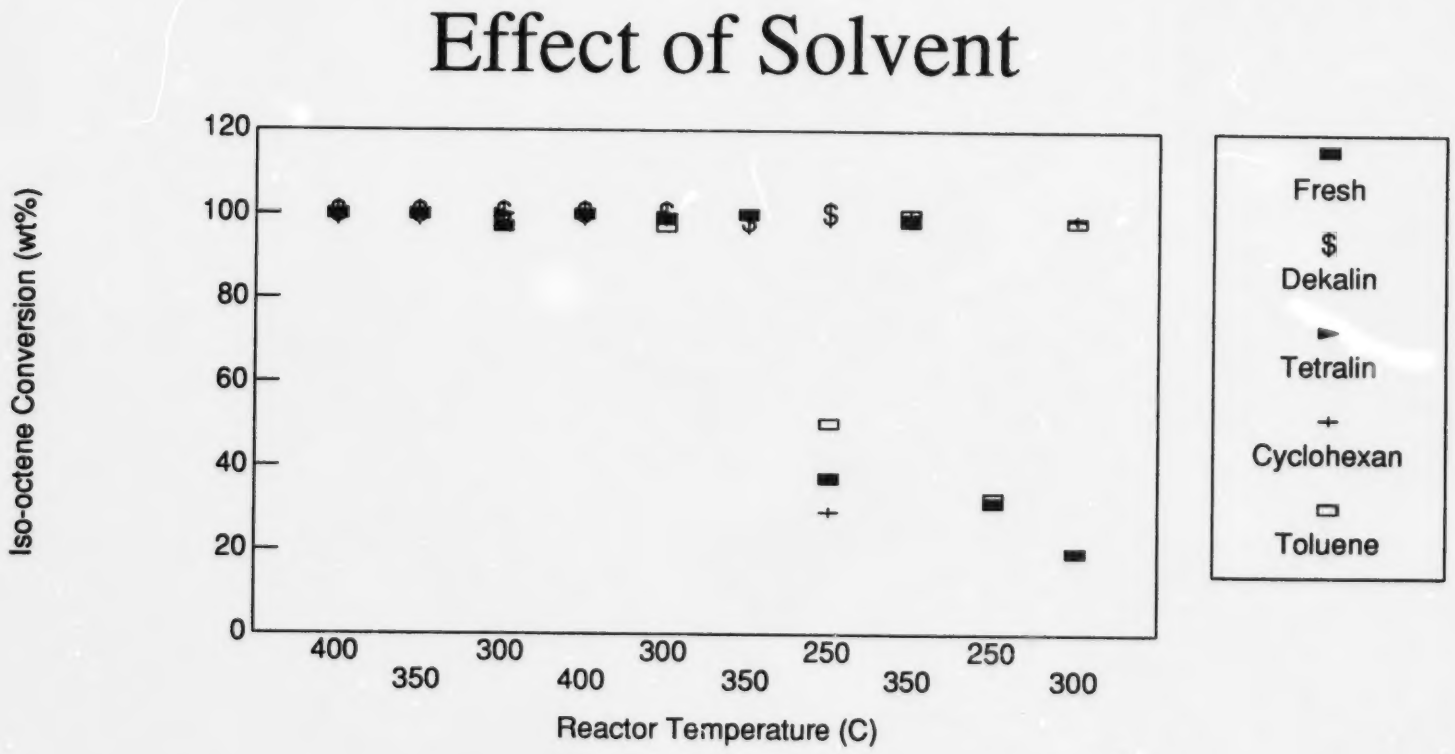
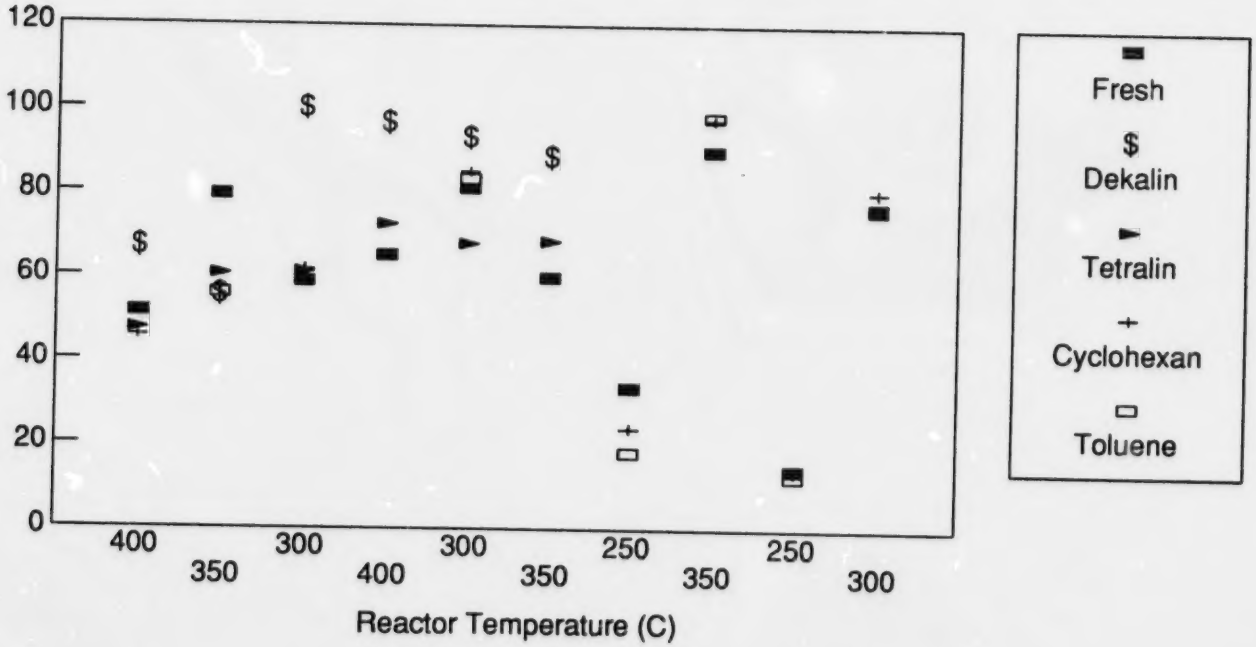


Figure 10: SULPHUR CONVERSION

Effect of Solvent



Sulphur conversion was not reduced by the impregnations: in several instances the sulphur conversion was actually improved over the fresh catalyst.

3.4 Effects of Impregnating the Harshaw Catalyst

The Harshaw catalyst was impregnated at a limited number of conditions. It was impregnated with a 9 wt % asphaltene in dekalin solution in the batch autoclave at the following conditions:

1. 22°C, atmospheric pressure;
2. 22°C, 6.9 MPa;
3. 200°C, atmospheric pressure;
4. 200°C, 7.2 MPa.

All the impregnations were done under an inert atmosphere. The catalysts were presulphided in the same manner as the HDS-20 in the hydroprocessing unit.

The corresponding activity measurement series were HARF (fresh), HAR1 (200°C, 7.2 MPa), HAR2 (200°C, atm), HAR3 (22°C, 6.9 MPa) and HAR4 (22ZC, atm). The cyclohexene, iso-octene and sulphur conversion data are compared graphically in Figures 14, 15 and 16. In each case it is readily apparent that the impregnation had minimal effect on the catalyst's activity. There are points on each graph indicating that the impregnated catalyst had a slightly greater activity than the fresh catalyst.

3.5 Activity Measurements of F145 Catalyst

Fresh and deactivated F145 catalyst was supplied by the CANMET scientific authority for the project. The intent was to compare the deactivation of the impregnated catalyst with catalysts that had been deactivated through hydrocracking of heavy oils.

Figure 11: CYCLOHEXENE CONVERSION

Effect of Temperature and Pressure

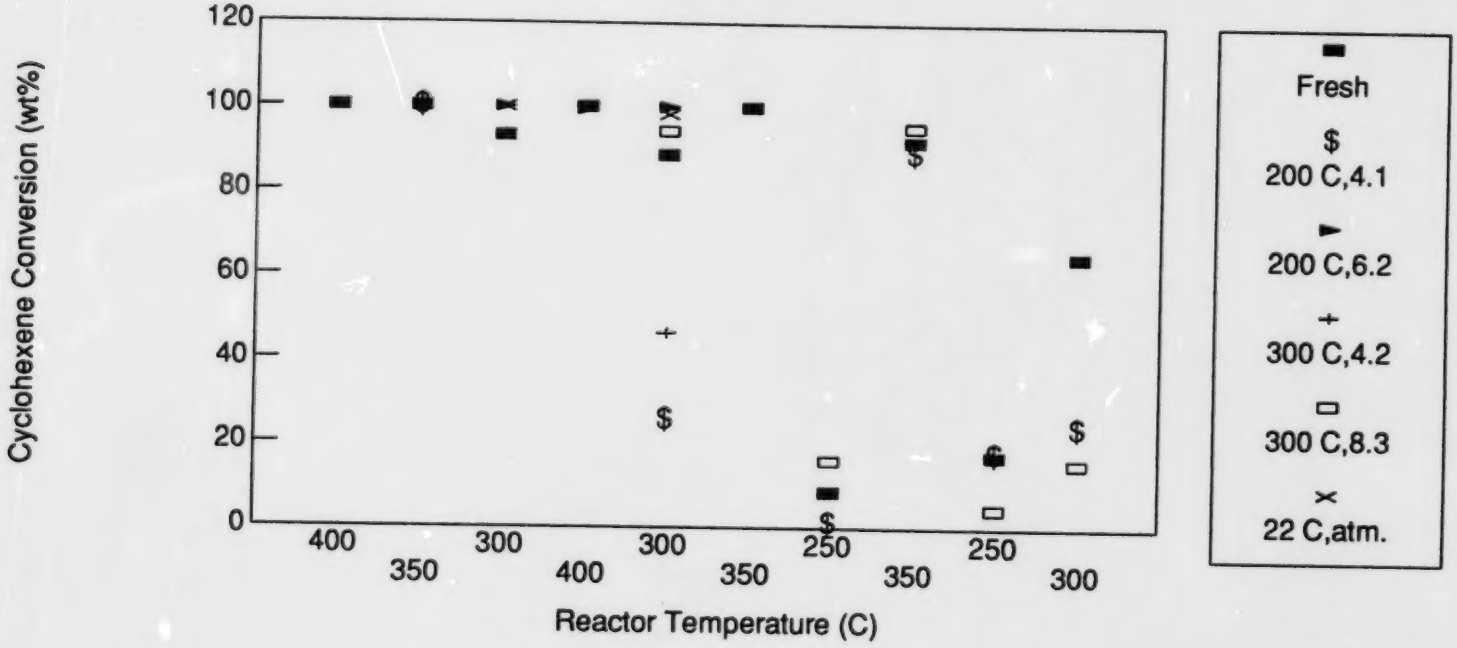


Figure 12: ISO-OCTENE CONVERSION

Effect of Temperature and Pressure

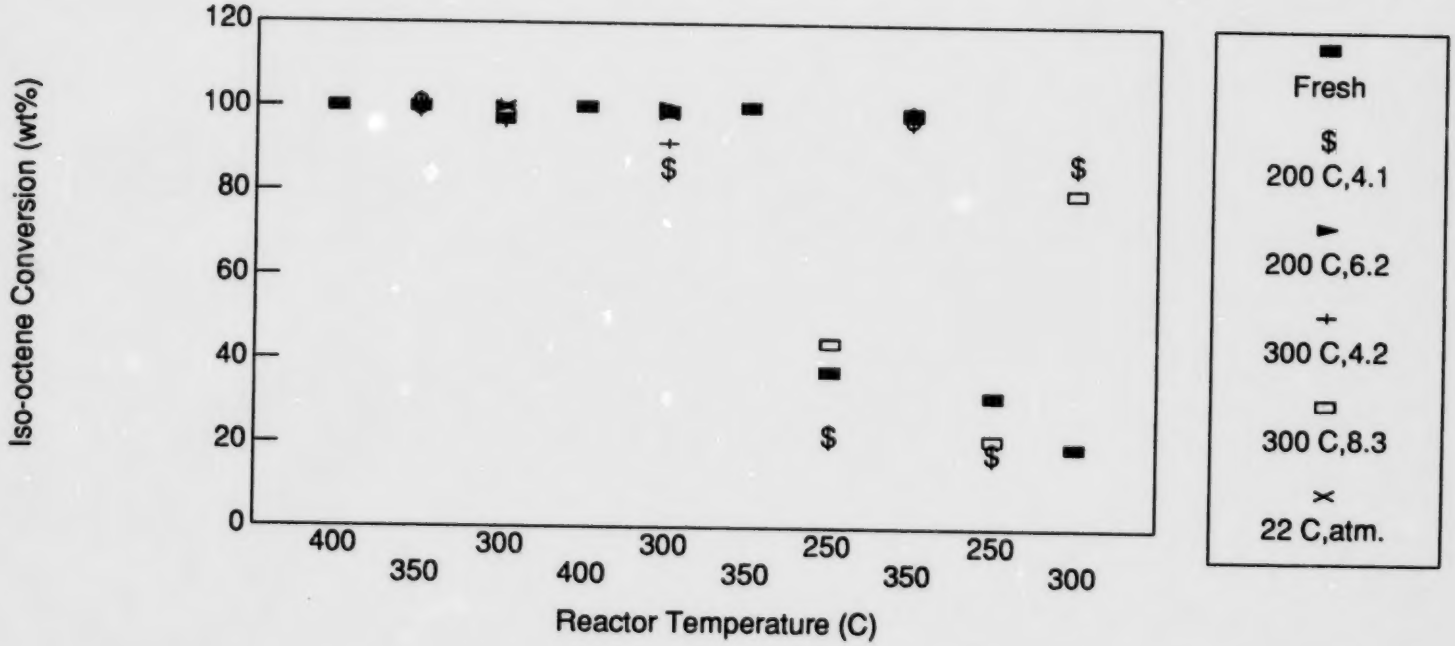


Figure 13: SULPHUR CONVERSION

Effect Of Pressure and Temperature

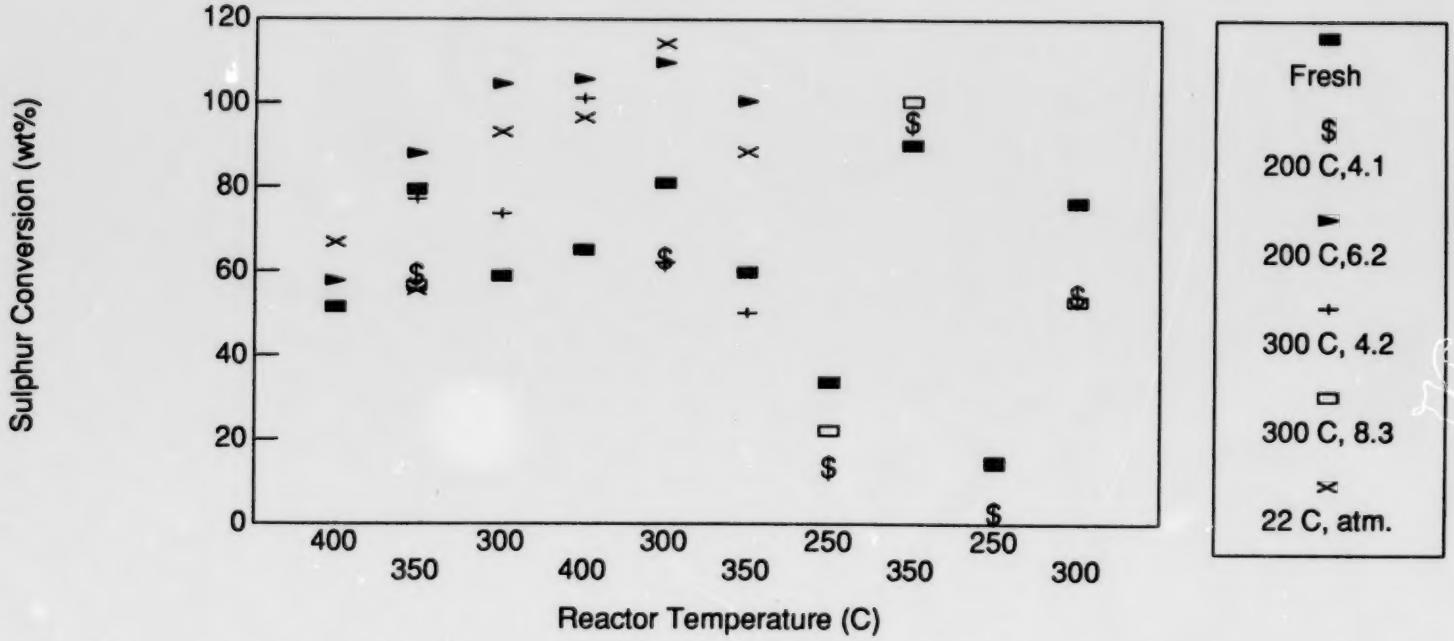


Figure 14: CYCLOHEXENE CONVERSION

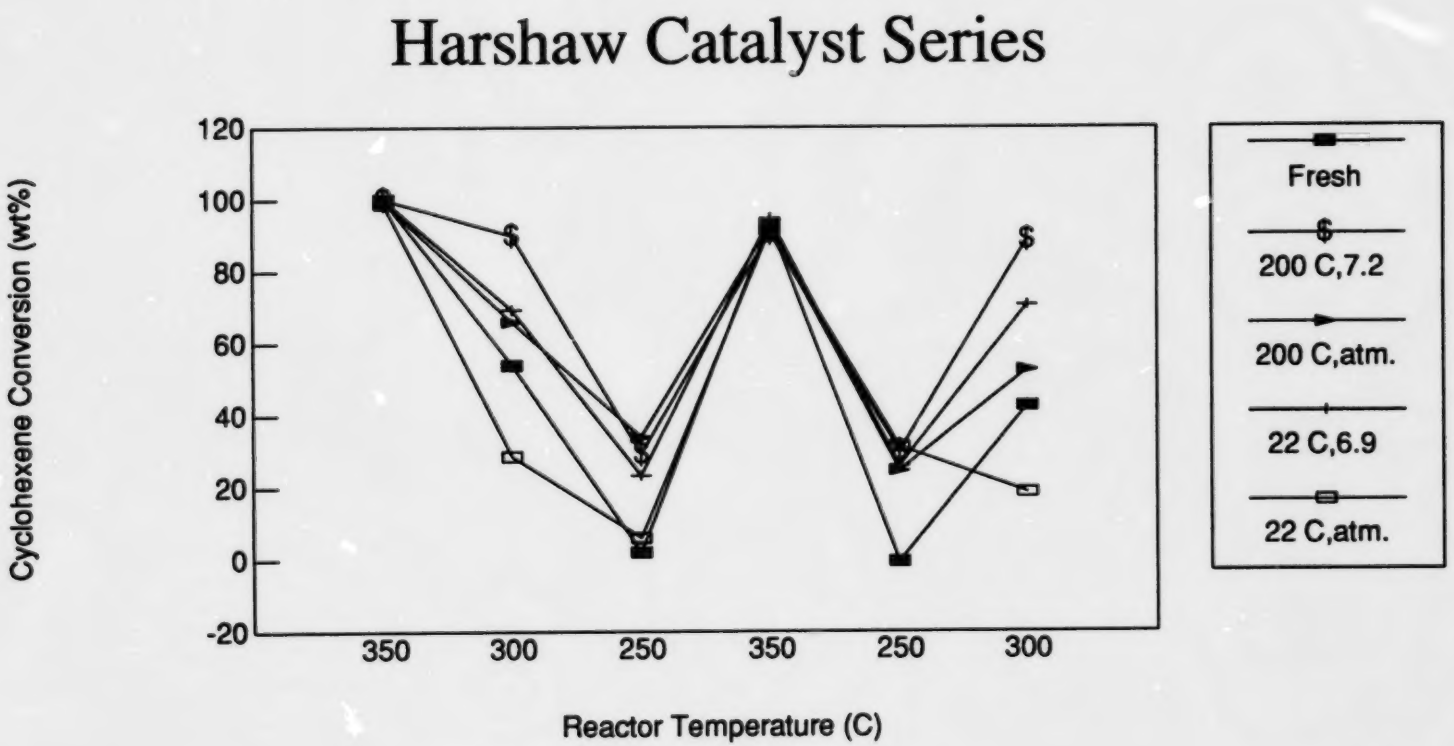


Figure 15: ISO-OCTENE CONVERSION

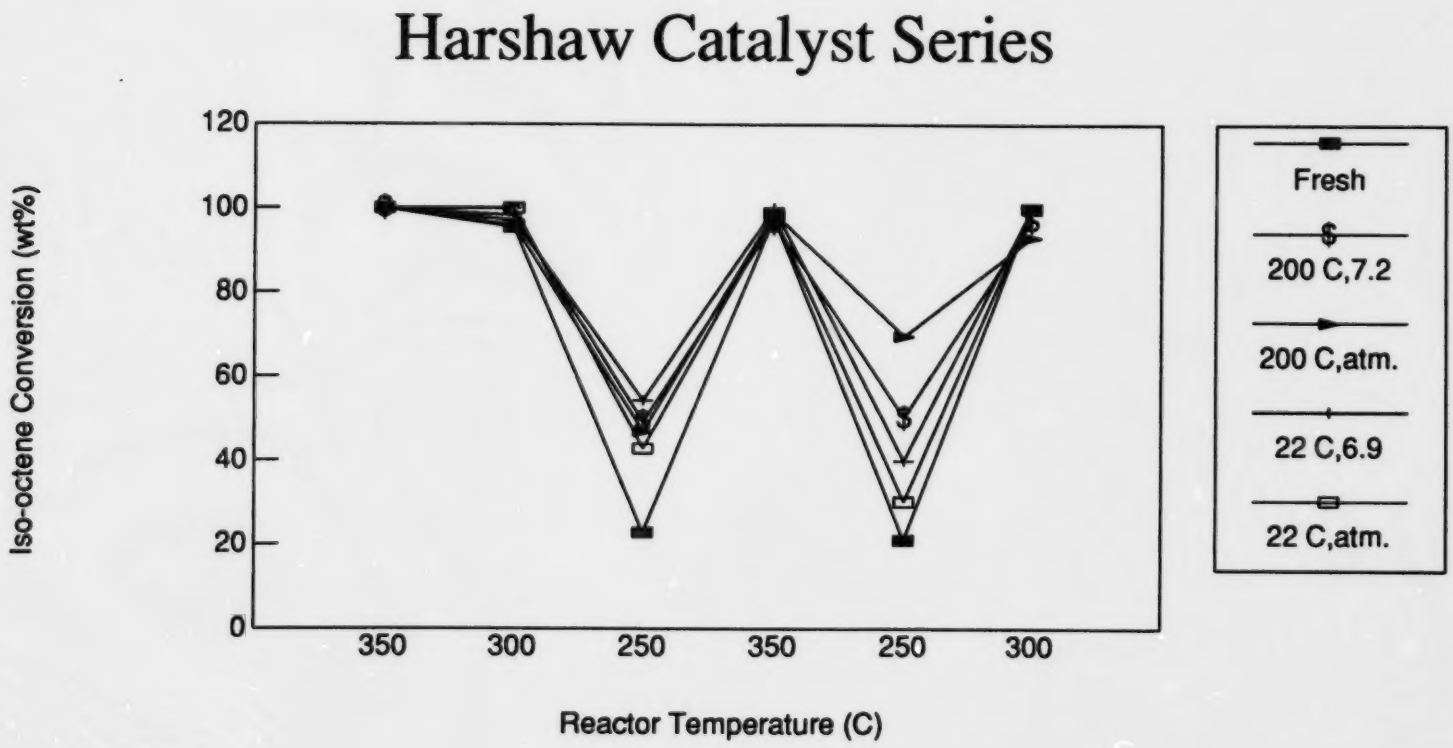
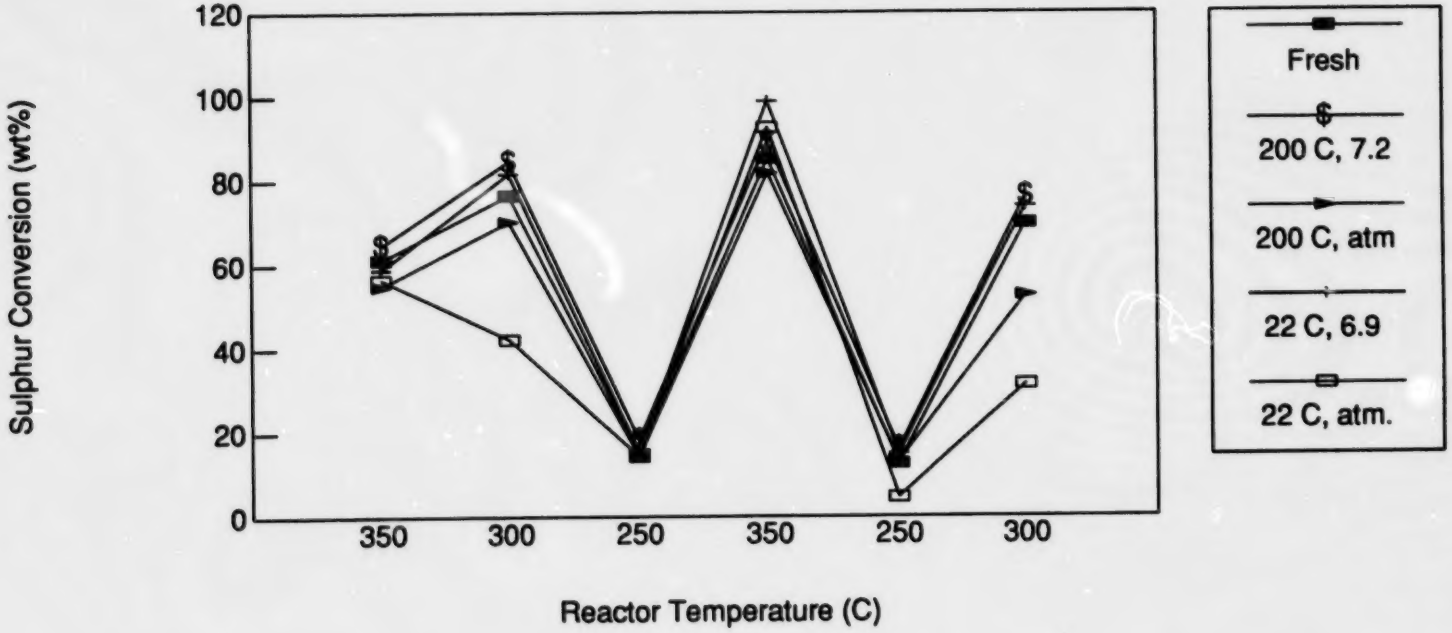


Figure 16: SULPHUR CONVERSION

Harshaw Catalyst Series



As the deactivated F145 catalyst was in powder form, the fresh F145 was ground using a mortar and pestel to approximately the same particle size prior to activity testing. Both catalysts were presulphided using the same procedure as the impregnated HDS-20 catalyst.

Figures 17, 18 and 19 compare some of the conversion data. The used F145 catalyst shows significant remaining activity in all the comparisons. Although the used F145 is typically reduced in activity, the difference is not as dramatic as expected.

3.6 Activity of Deactivated HDS-20 Catalyst

SRC supplied a sample of deactivated HDS-20 from hydrocracking Lloydminster atmospheric resid. The time on stream for the catalyst was approximately 300 hours at high resid conversion conditions. The sample catalyst retained almost no activity at the end of the hydrocracking experiment. Conversion and desulphurization were down to thermal hydrocracking levels when the hydrocracking experiment was ended.

Figures 20, 21 and 22 compare conversion data of the deactivated HDS-20 and fresh HDS-20. Similar to the F145 results, the used HDS-20 showed remarkable activity with the model compound feedstock especially at the higher pressure and temperature conditions. Only at the lower temperature conditions did the used HDS-20 show any significant reduction in activity.

3.7 Catalyst Presulphiding

The normal catalyst presulphiding procedure used by the Saskatchewan Research Council was not suitable for the purpose of this project. The procedure, obtained from a commercial catalyst supplier, uses a light virgin (non-thermally altered) gas oil mixed with carbon disulphide (CS_2) as the sulphur source. The procedure requires approximately 16 hours to complete because it needs several steps of increasing temperature. It was

Figure 17: CYCLOHEXENE CONVERSION

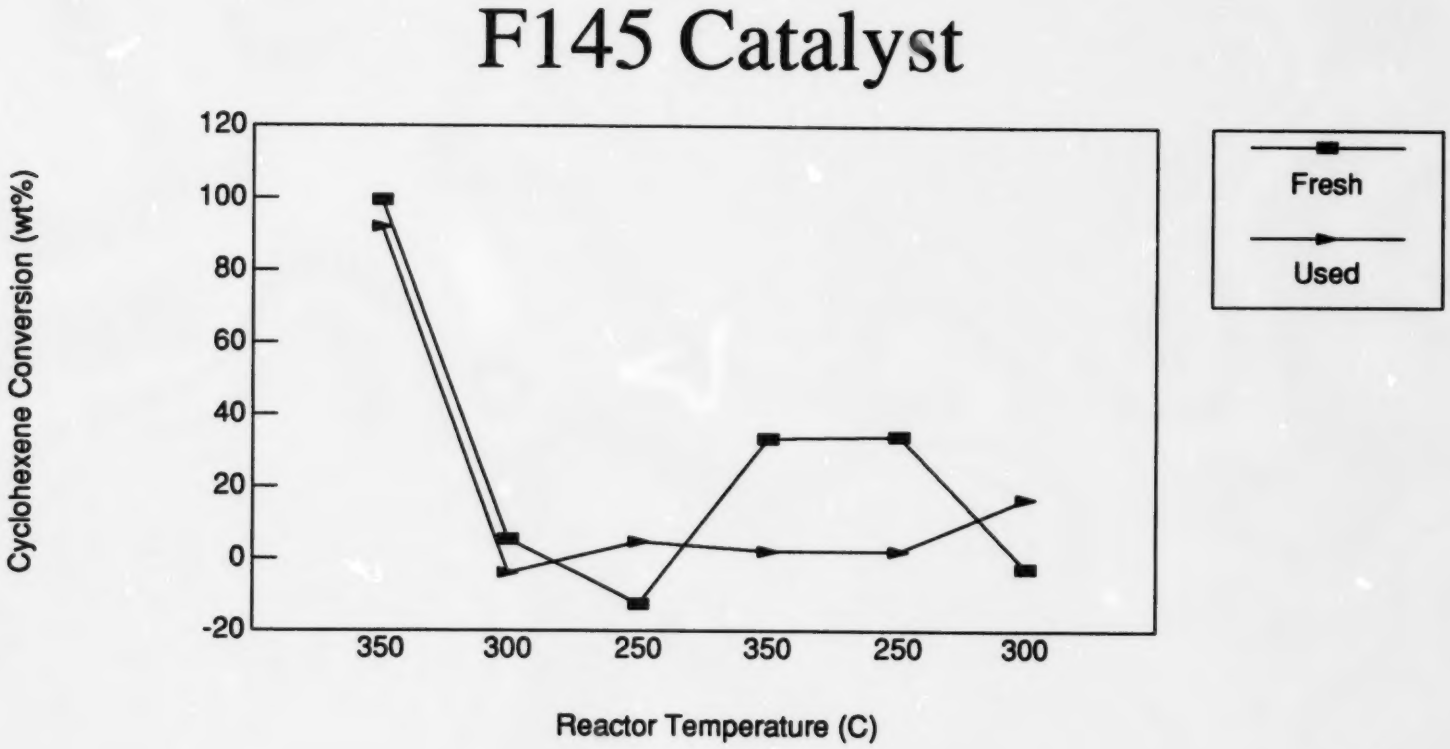


Figure 18: ISO-OCTENE CONVERSION

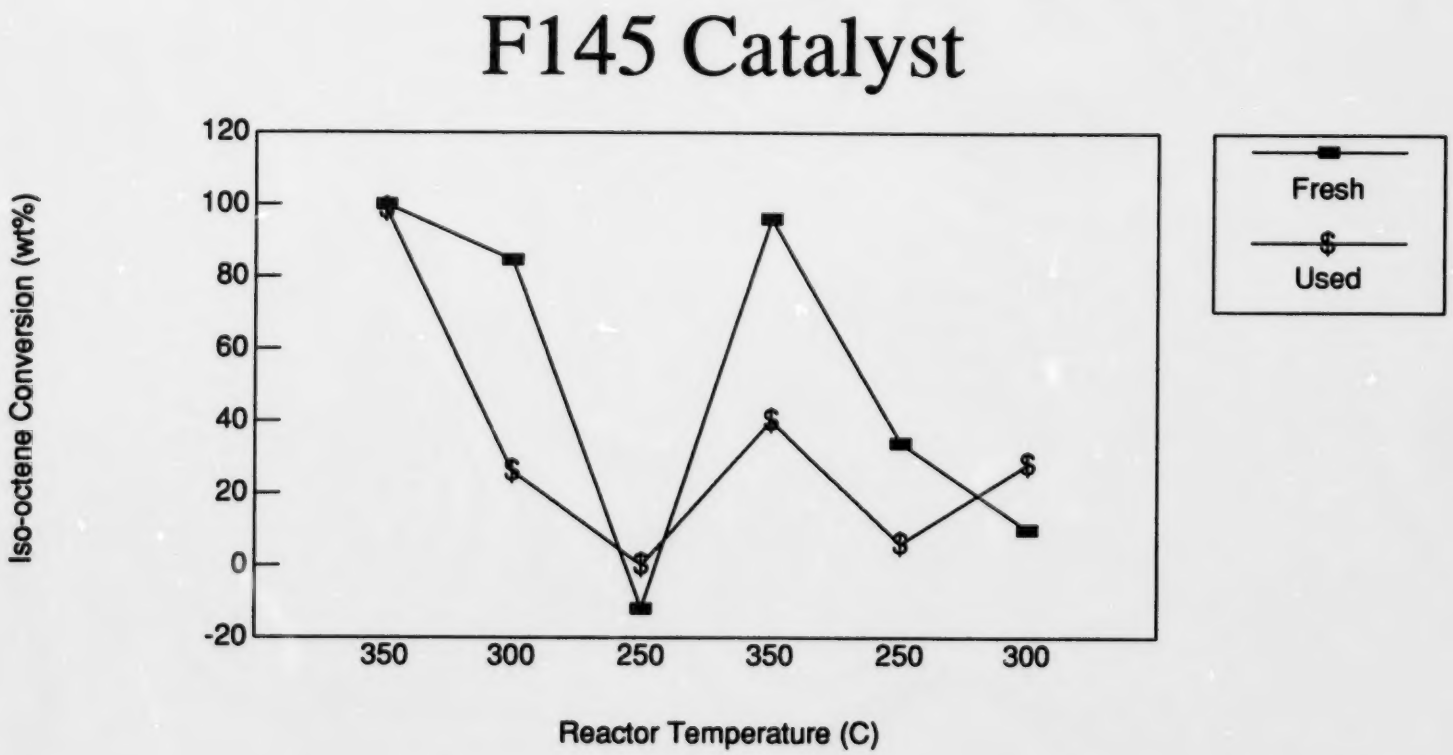


Figure 19: SULPHUR CONVERSION

F145 Catalyst

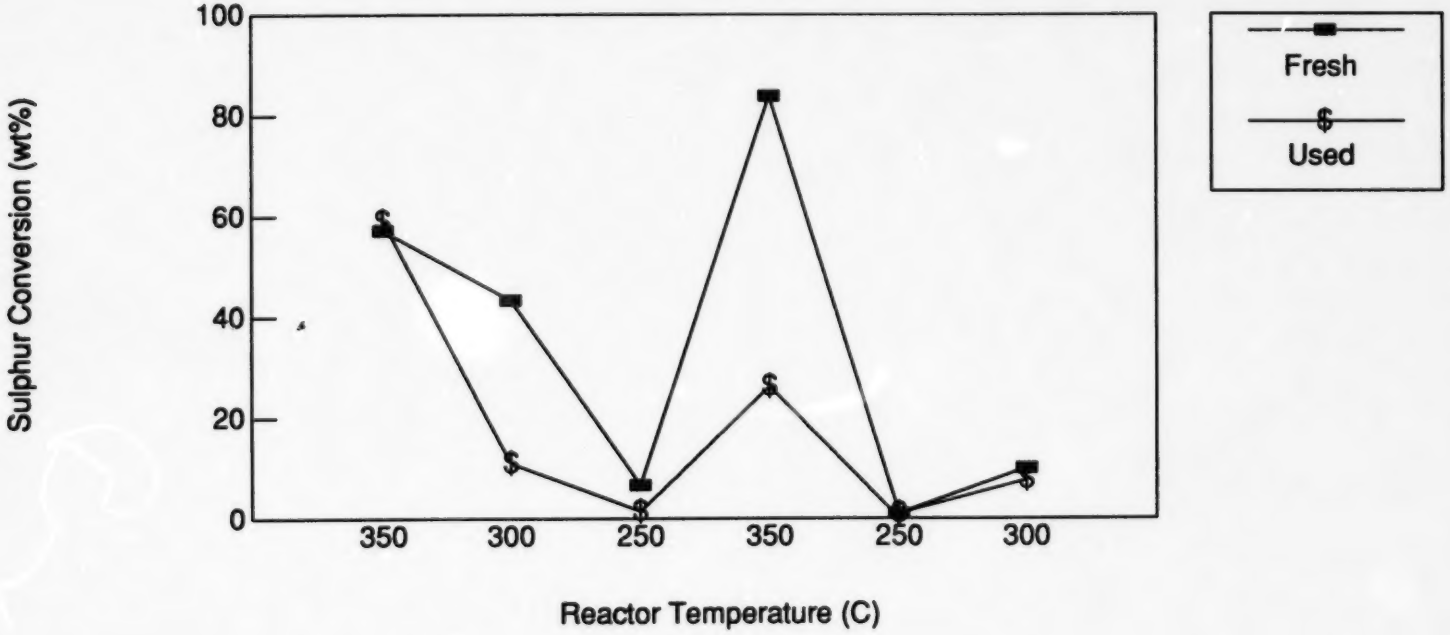


Figure 20: CYCLOHEXENE CONVERSION

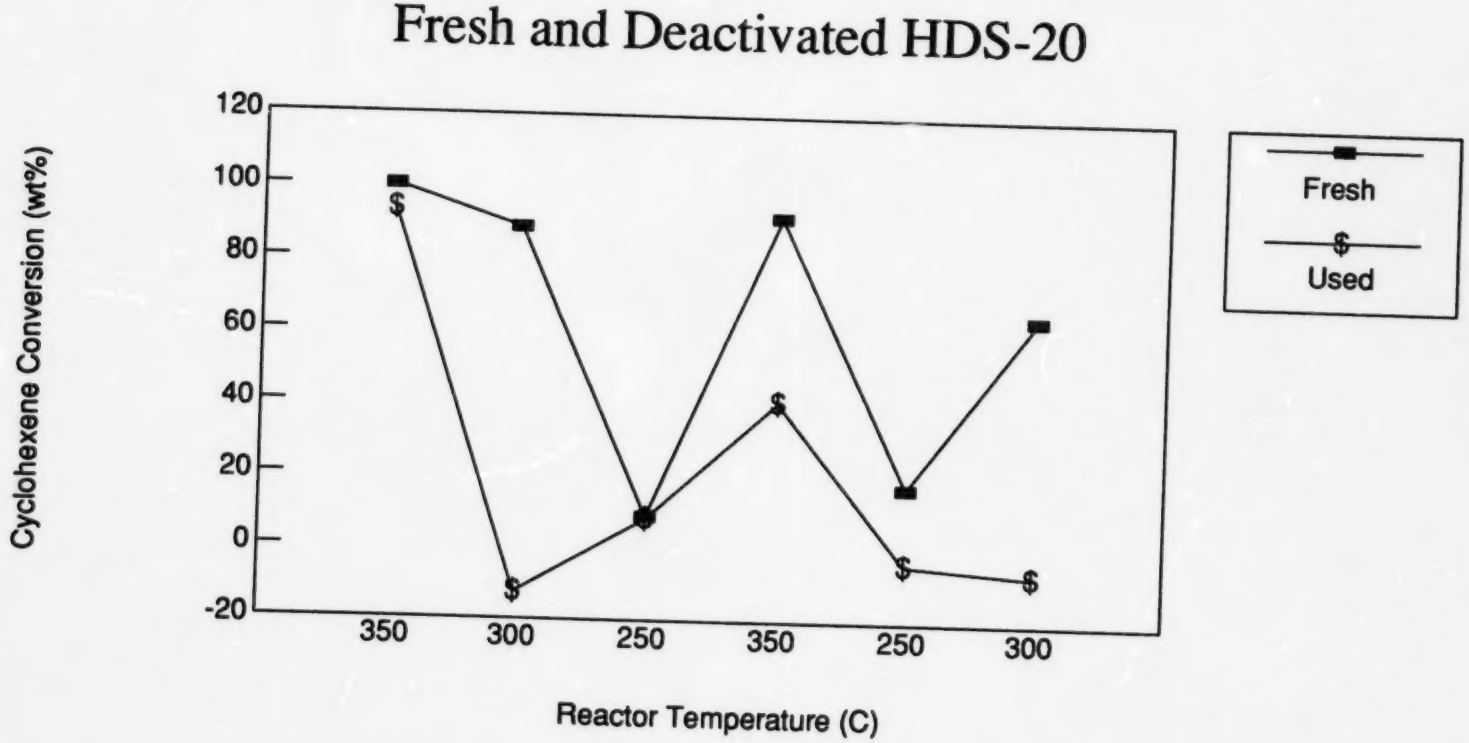


Figure 21: ISO-OCTENE CONVERSION

Fresh and Deactivated HDS-20

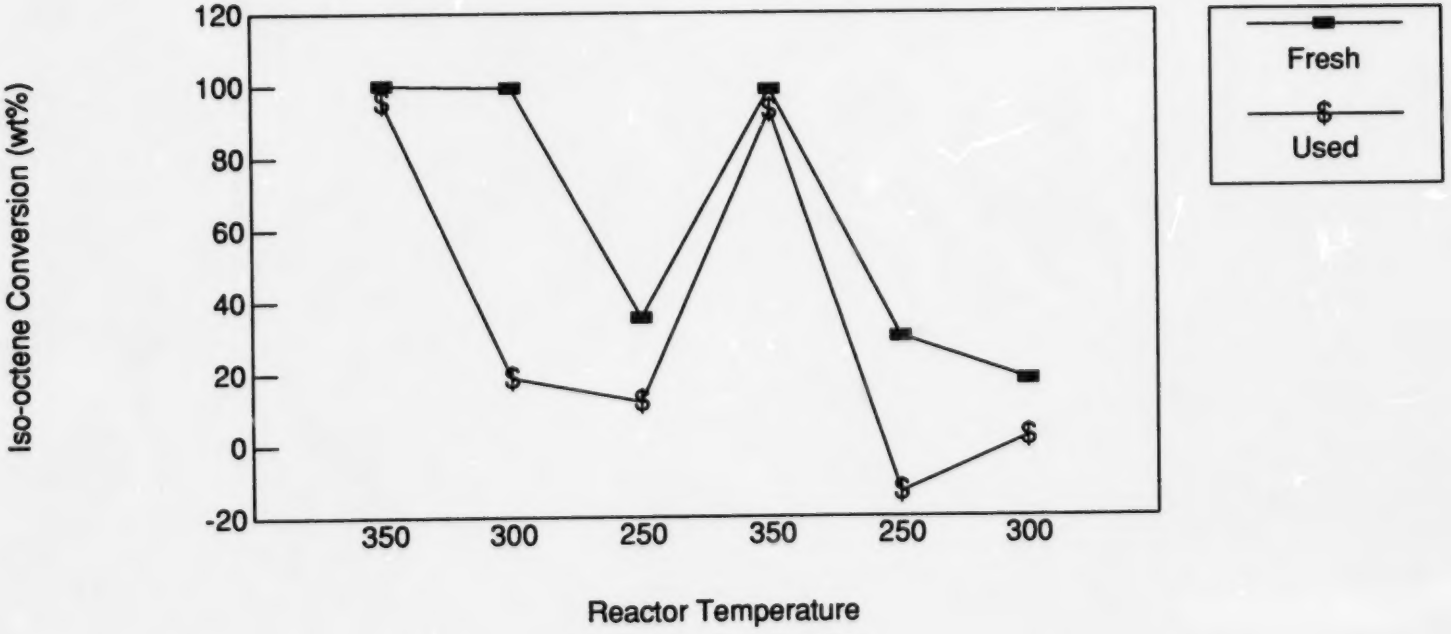
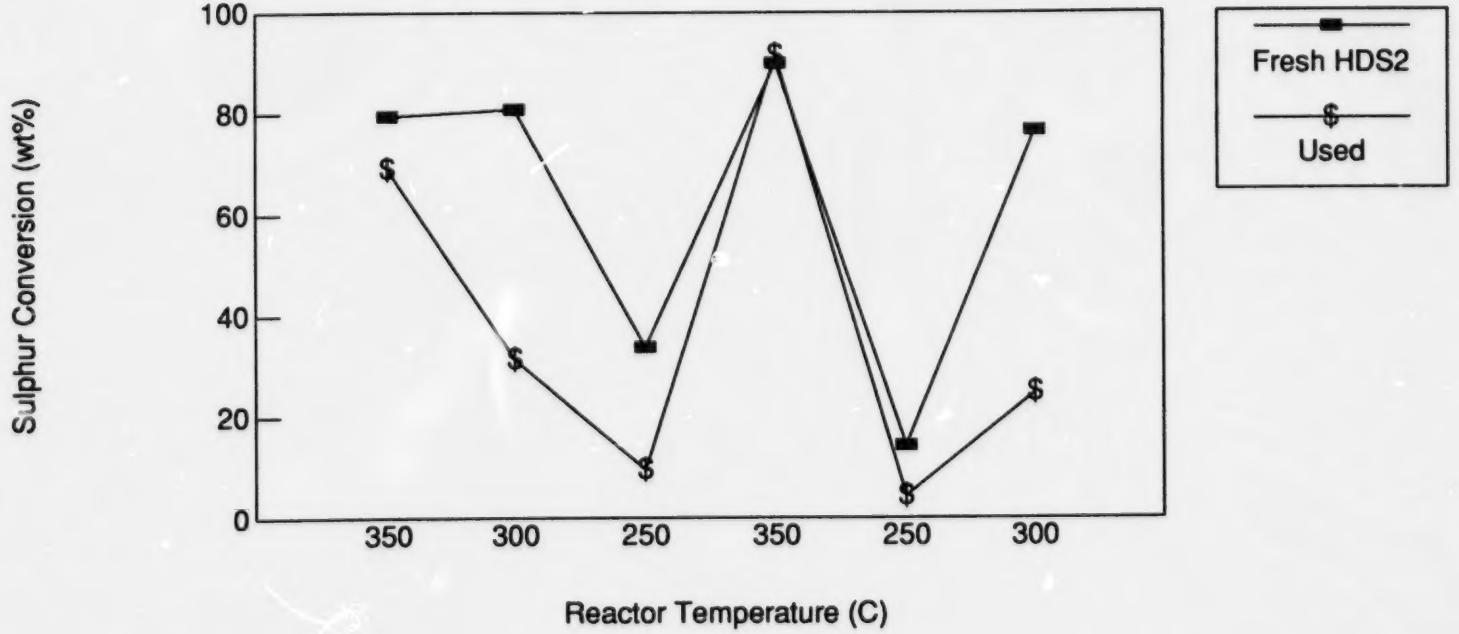


Figure 22: SULPHUR CONVERSION

Fresh and Deactivated HDS-20



unsuitable for this project because the liquid feedstock would contaminate the unit for the model compound feedstock. Also, the lengthy period to presulphide would add significant labour and time requirements to complete the project considering the number of catalysts to be presulphided.

The literature provided an alternative presulphiding technique, which appeared to be satisfactory in that it had been used by the majority of researchers. The procedure used H_2S in H_2 as the sulphur source. The catalyst was usually treated for 2-4 hours at 400°C and atmospheric pressure. The amount of H_2S fed provided approximately two to four times the sulphur required by the catalyst. None of the articles indicated any problems with the procedure.

The procedure seemed ideally suited for the purposes of the project as it eliminated the liquid feedstock and the time required for presulphiding was drastically reduced. The first experiment performed indicated that the catalyst was not adequately presulphided. This was shown by the long period required for the product gas composition to stabilize. It was expected, and has been SRC's experience with the small laboratory-scale units, that equilibrium is achieved relatively rapidly (usually within an hour). The composition was still not stable after four hours of operation.

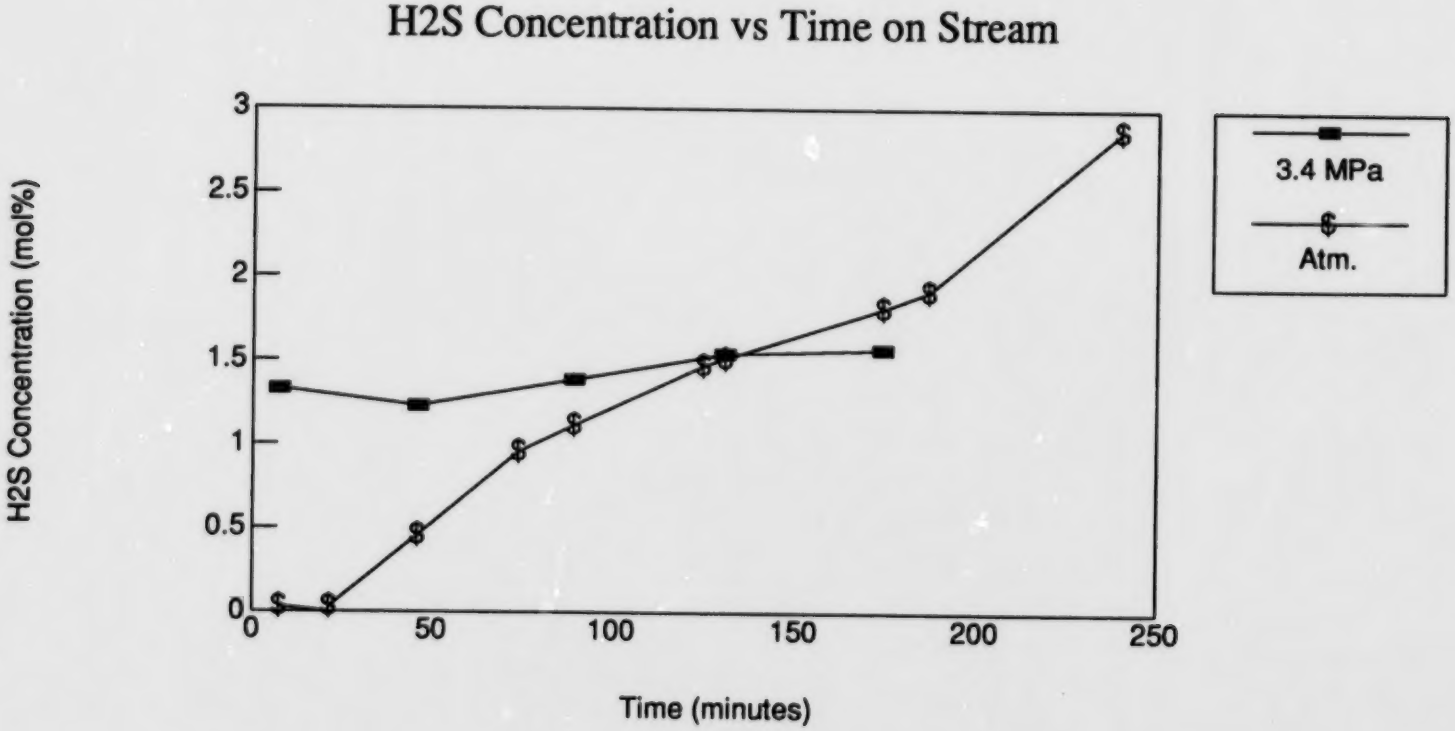
Other alternatives were considered and tried. In the subsequent catalyst series an additional experiment was performed at 400°C with the model compound feedstock to complete presulphiding. This was adequate but the extra experiment added another day of operation to each catalyst series. There is some discussion in the literature as to the necessity of presulphiding at all with a high sulphur feedstock. Although there may be some validity to the argument, it is not supported by catalyst manufacturers so the option was not pursued in this project. Another suggested alternative was to presulphide with H_2S at a higher pressure. In the next series the catalyst was presulphided at 400°C and 3.4 MPa. The catalyst was adequately presulphided using this technique, subsequent gas compositions stabilized 1 to 1.5 hours into the experiment.

Figure 23, Comparison of Presulphiding Methods, graphically illustrates the differences between the presulphiding techniques. Both lines are from the first experiment after the completion of presulphiding. The H_2S concentration is plotted against time on stream for the particular experiment. The hydrotreating conditions are the same for both curves, 400°C and 6.9 MPa. One curve is for presulphiding at atmospheric pressure while the other is presulphided at 3.4 MPa. It is clear that the catalyst presulphided at 3.4 MPa achieves equilibrium much quicker than the other catalyst. The activity of the catalyst is also much stabler than the atmospheric pressure presulphiding.

3.8 Effect of Presulphiding on the Impregnated Asphaltenes

Near the end of the experimental series, when it was apparent that the asphaltene impregnations were having a limited effect on activity, a simple test was tried to determine the effect of presulphiding on the impregnated asphaltenes. It was noticed that during presulphiding a small amount of hydrocarbon was present in the product gas. A batch of Harshaw catalyst was impregnated with a 9 wt % asphaltene in dekalin solution at 200°C and 9.2 MPa. Part of the catalyst was presulphided in the normal manner, at 400°C and 3.4 MPa with a 10% H_2S in H_2 gas mixture. The presulphided catalyst and the unpresulphided catalyst were then analyzed for carbon and hydrogen content. The presulphided catalyst had 1.9 wt % carbon, 0.68 wt % hydrogen while the unsulphided catalyst contained 6.3 wt % carbon and 1.19 wt % hydrogen. Assuming the carbon and hydrogen were from the impregnated asphaltene, presulphiding removed almost 65%.

Fig.23: Presulphiding Method Comparison



IV. CONCLUSIONS AND RECOMMENDATIONS

The primary conclusions that can be drawn from this work include:

1. The project was unsuccessful in developing effective asphaltene impregnation techniques that would deactivate the catalyst in a similar manner to hydrocracking of heavy oils.

2. Presulphiding is very important in the preparation of catalyst for testing, especially for short-term tests.

3. Model compounds have limited application in the testing of catalytic activity.

4. Prior to testing a catalyst's activity, it is important that the catalyst be at a stable level of activity.

5. Presulphiding removed a majority of the impregnated asphaltenes.

6. Short experimental periods do not always allow the achievement of equilibrium, sometimes giving inconsistent results.

7. Determining sulphur conversion by H_2S production was not a consistent measure of sulphur removal.

8. The analytical technique for measuring unconverted components was too time-consuming and unreliable.

The data indicate that the asphaltene impregnations had only limited effect on catalytic activity and on occasion it improved activity. Denitrogenation activity was only slightly reduced from fresh catalyst samples. Desulphurization activity was affected in an inconsistent manner; there were several examples where desulphurization was improved after impreg-

nation. Hydrogenation activity did show some decrease in certain instances, but consistent results were not achieved.

One of the more significant results was the determination of the impact of the presulphiding technique on catalytic activity. The literature provided several presulphiding techniques, but none of the articles indicated any limitations with any of them. It is difficult to believe that inconsistent results were not a problem for several of the researchers. To reliably measure a catalyst's activity the catalyst must be at a stable activity plateau. The first step is to completely presulphide the catalyst.

Several catalysts indicated some activity instability by showing an increased activity later in the experimental series. This phenomenon has occurred in other catalyst testing performed by SRC. Commercial catalyst suppliers specify up to three days of operation using an unreactive feedstock to stabilize activity and maximize catalyst life. The second step in proper catalyst preparation should therefore include operation for a period of time, usually 24-48 hours, to allow the catalyst to settle down to a stable activity level.

Presulphiding did remove the majority of impregnated material. Impregnating after presulphiding may have made the impregnations more effective, but that is not a certainty. There are other possibilities that could reduce the asphaltene concentration on the catalyst and hence the impact of the material on activity. The aromatic components in the feedstock may extract some of the asphaltene material from the catalyst under hydrotreating conditions. With no asphaltene component in the feed, the asphaltenes may dissolve into the feed until some equilibrium concentration is achieved. Some of the asphaltene material may also become converted during the hydrotreating experiments, gradually reducing it to an insignificant level. These potential effects need to be studied in future work.

The results show that the catalyst did not respond to the model compound mixture in the same manner as a petroleum feedstock. These data question the validity of using a model compound feed to test catalytic activity. The mixture was designed to have a similar makeup to a heavy oil feedstock. At normal hydrotreating conditions the two deactivated catalysts had comparable activity to the fresh catalyst samples. Only at much lower severity conditions did any activity differences begin to appear. It may be possible to correlate the low severity results with the model compound mix with operation at high severity and a petroleum feedstock, but not without a great deal of experimentation. There are interactions between the components in the feedstock that are not quantifiable and hence, it is difficult to construct a model compound mixture that responds in a similar manner to petroleum feedstock. To reliably test catalytic activity, a standardized petroleum feedstock may provide more appropriate and reliable results.

There are advantages in a simple model compound mix, such as simplified analysis and accurate determination of the hydrotreating effectiveness of the simple mixture. In this case the original complex mixture may have been more suitable, but the analysis was too complex for the available equipment. If there had been other analytical capabilities available, such as a mass spectrophotometer, analysis may have been easier. Such capabilities are expensive and the potential benefits must be evaluated against the cost.

The short experimental period contributed to some inconsistent results. Most experiments were 3-4 hours long with a few periods lasting five hours. The gas composition took almost half of the period to stabilize. An average gas composition was used to calculate gas yield and sulphur conversion. Errors were significant because the initial period was included in the calculations. The longer experiments were better because longer steady state operation was achieved. Only one long experiment was possible in a day, but two of the shorter ones were feasible. The extra

time spent will yield more reliable data, which in turn translates into extra time and budget requirements to perform the same number of experiments.

Sulphur conversion was determined from gas analysis and gas volume measurements. This was not suitable because of the short experiment length. The most reliable method would be to perform liquid sulphur analysis and determine conversion from that analysis.

The liquid products were analyzed for unconverted components using a capillary column gas chromatograph. The work was very time-consuming and frequently required more than one repeat analysis. Interference from some of the conversion products was suspected as the cause of the inconsistent analysis, but it was not conclusively determined. Mass spectrophotometer analysis would be more suitable in analyzing a complex mixture of components, identification of the components would be simplified.

Although the results are inconclusive regarding the effect of asphaltene adsorption on catalyst activity, the idea is not without merit. A number of the problems identified with the methods used in this project could be avoided and some of the other potential effects measured without extensive experimentation. A more definitive answer is possible with longer experiments using a stable activity catalyst and a more appropriate feedstock.

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APPENDIX I

TABLES

TABLE 1. HDS-20 Catalyst, Asphaltene Impregnation by Physical Mixing at Ambient Conditions

Exp No.	8701AA	8701AB	8701AC	8701AD	8701AE	8701AF	8701AG
Impregnation Conditions	Solvent: Dekalin Temperature: 22°C			Asphaltene Content: 9 wt % Pressure: atm			
Hydrotreating							
Temp (°C)	400	350	300	400	400	300	350
Press (MPa)	6.9	5.2	3.4	3.4	6.9	6.9	5.2
Yield Summary							
Liquid (wt % feed)	86.7	77.2	106.8	86.1	70.1	73.9	89.0
Gas (wt % feed)	8.7	5.1	9.2	10.2	10.7	11.0	11.3
H_2 Consumption	0.0116	0.0056	0.0035	0.0039	0.0061	0.0048	0.0180
Sulphur Conv %	66.6	55.4	93.2	96.3	89.1	113.9	88.6
Gas Analysis							
H_2	93.271	96.903	95.135	94.775	94.960	93.923	91.540
C_3H_8	0.027	0.008		0.044	0.018	0.003	0.015
C_3H_6							
H_2S	2.889	1.765	2.645	2.623	2.298	3.314	3.555
$i\text{-}C_4H_{10}$	0.281	0.024	0.022	0.203	0.225	0.090	0.189
$n\text{-}C_4H_{10}$	3.273	1.168	2.077	2.169	2.359	2.548	3.921
$t\text{-}C_4H_8$							
$c\text{-}C_3H_8$							
C_2H_6	0.016			0.022	0.002		0.010
N_2	0.205	0.131	0.122	0.095	0.110	0.122	0.750
CH_4	0.038			0.069	0.027		0.021
Liquid Analysis (wt % of feed)							
Thiophene	0.00	0.00	0.00	0.00	0.00	0.17	0.01
Cyclohexane	32.27	27.95	37.31	27.78	24.33	24.83	32.91
Cyclohexene	0.00	0.00	0.00	0.00	0.01	0.24	0.02
Isoctene	0.00	0.00	0.00	0.00	0.00	0.17	0.01
Toluene	24.85	24.88	36.38	25.98	20.83	25.90	29.62
Napthalene	0.16	0.08	3.82	0.96	0.20	0.61	0.30
Quinoline	0.03	0.00	0.00	0.01	0.00	0.00	0.00
Conversion (wt %)							
Thiophene	100.00	100.00	100.00	100.00	100.00	98.29	99.91
Cyclohexane	-24.45	-7.78	-43.87	-7.15	6.16	4.24	-26.93
Cyclohexene	100.00	100.00	100.00	100.00	99.95	98.18	99.87
Isoctene	100.00	100.00	100.00	100.00	100.00	98.30	99.91
Toluene	17.03	16.92	-21.46	13.35	30.53	13.60	1.20
Naphthalene	97.64	98.78	45.22	86.32	97.22	91.30	95.71
Quinoline	99.04	100.00	100.00	99.76	100.00	100.00	100.00

TABLE 2. HDS-20 Catalyst, Physical Mixing at 100°C

Exp No.	8701BA	8701BB	8701BC	8701BD	8701BE	8701BF
Impregnation Conditions	Solvent: Dekalin		Asphaltene Content: 9 wt %			
	Temperature: 100°C		Pressure: atm			
Hydrotreating						
Temp (°C)	400	350	300	400	300	350
Press (MPa)	6.9	5.2	6.9	3.4	3.4	5.2
Yield Summary						
Liquid (wt % feed)	94.4	83.8	98.0	103.2	96.2	97.8
Gas (wt % feed)	10.4	11.3	8.2	8.8	9.2	8.3
H_2 Consumption	0.0034	0.0118	0.0082	0.0118	0.0089	0.0129
Sulphur Conv %	89.9	82.7	78.9	76.8	87.2	73.5
Gas Analysis						
H_2	89.995	94.407	95.794	95.024	95.042	94.698
C_3H_8	0.036	0.004		0.018		0.004
C_3H_6						
H_2S	4.736	2.331	2.180	2.369	2.535	2.580
i-C_4H_{10}	0.340	0.046	0.015	0.111		0.063
n-C_4H_{10}	4.683	3.141	1.952	2.357	2.142	2.618
1-C_4H_8					0.038	
i-C_4H_8			0.007		0.127	
t-C_4H_8			0.001		0.083	
c-C_3H_8						
C_2H_6	0.024			0.028		
N_2	0.185	0.171	0.051	0.068	0.033	0.038
CH_4	0.040			0.025		
Liquid Analysis (wt % of feed)						
Thiophene	0.12	0.00	0.00	0.11	0.13	0.00
Cyclohexane	35.58	31.10	34.31	37.51	34.21	37.83
Cyclohexene	0.14	0.00	0.06	0.37	0.88	0.00
Isoctene	0.03	0.00	0.00	0.10	0.06	0.00
Toluene	29.95	28.59	30.83	34.14	32.93	32.77
Napthalene	0.72	0.28	4.77	3.80	7.03	0.46
Quinoline	0.00	0.00	0.00	0.00	0.00	0.00
Conversion (wt %)						
Thiophene	98.80	100.00	100.00	98.90	98.60	100.00
Cyclohexane	-37.30	-20.00	-32.40	-44.70	-32.00	-46.30
Cyclohexene	98.90	100.00	99.60	97.20	93.50	100.00
Icoctene	99.70	100.00	100.00	99.00	99.40	100.00
Toluene	0.00	4.60	-2.90	-13.90	-9.90	-9.40
Naphthalene	90.00	96.10	33.30	46.90	1.60	93.60
Quinoline	100.00	100.00	100.00	100.00	100.00	100.00

TABLE 3. HDS-20 Catalyst, Physical Mixing at 200°C

Exp No.	8701CA	8701CB	8701CC	8701CD	8701CE	8701CF
Impregnation Conditions	Solvent: Dekalin Temperature: 200°C			Asphaltene Content: 9 wt % Pressure: atm		
Hydrotreating						
Temp (°C)	400	350	300	400	300	350
Press (MPa)	6.9	5.2	6.9	3.4	3.4	5.2
Yield Summary						
Liquid (wt % feed)	93.0	110.4	104.3	100.1	92.9	91.3
Gas (wt % feed)	6.1	7.8	5.5	10.0	5.3	4.3
H_2 Consumption	0.0067	0.0058	0.0079	0.0156	0.0113	0.0114
Sulphur Conv %	56.9	71.5	63.5	89.3	74.0	61.4
Gas Analysis						
H_2	95.777	95.194	95.326	94.197	97.014	97.095
C_3H_8	0.013	0.004		0.021		0.003
C_3H_6						
H_2S	2.123	2.405	2.783	2.846	2.065	2.038
$i\text{-}C_4H_{10}$	0.129	0.049	0.033	0.132		0.014
$n\text{-}C_4H_{10}$	1.870	2.314	1.682	2.719	0.751	0.812
$1\text{-}C_4H_8$			0.031		0.031	
$i\text{-}C_4H_8$						
$t\text{-}C_4H_8$					0.068	
$c\text{-}C_3H_8$					0.029	
C_2H_6	0.008			0.014		
N_2	0.061	0.034	0.046	0.044	0.043	0.038
CH_4	0.021			0.028		
Liquid Analysis (wt % of feed)						
Thiophene	0.00	0.00	0.37	0.00	0.26	0.00
Cyclohexane	33.67	39.26	33.72	35.73	29.55	33.66
Cyclohexene	0.00	0.00	1.27	0.00	1.30	0.00
Isoctene	0.00	0.00	0.42	0.00	0.14	0.00
Toluene	25.88	33.83	32.15	30.32	25.55	27.01
Napthalene	0.25	0.60	7.75	1.10	5.23	0.47
Quinoline	0.01	0.00	1.10	0.02	0.54	0.28
Conversion (wt %)						
Thiophene	100.00	100.00	96.40	100.00	97.40	100.00
Cyclohexane	-29.70	-51.20	-29.90	-37.60	-13.80	-29.70
Cyclohexene	100.00	100.00	90.50	100.00	90.30	100.00
Isoctene	100.00	100.00	95.80	100.00	98.60	100.00
Toluene	13.30	-13.40	-7.70	-1.60	-14.40	9.50
Naphthalene	96.40	91.50	-10.70	84.30	25.30	93.20
Quinoline	99.80	100.00	71.00	99.50	85.70	92.50

TABLE 4. HDS-20 Catalyst, Physical Mixing at Ambient Conditions with 17% Asphaltene Concentration

Exp No.	8701DA	8701DB	8701DC	8701DD	8701DE	8701DF
Impregnation Conditions	Solvent: Dekalin Temperature: 22°C			Asphaltene Content: 17 wt % Pressure: atm		
Hydrotreating						
Temp (°C)	400	350	400	300	300	350
Press (MPa)	6.9	5.2	3.4	3.4	6.9	5.2
Yield Summary						
Liquid (wt % feed)	91.0	91.5	73.1	83.3	95.2	71.2
Gas (wt % feed)	4.4	5.0	6.3	5.1	3.8	4.6
H_2 Consumption	0.0085	0.0075	0.0073	0.0031	0.0008	0.0061
Sulphur Conv. %	53.1	65.0	74.5	70.9	54.9	61.3
Gas Analysis						
H_2	97.894	97.587	96.855	97.590	98.030	97.163
C_3H_8	0.009	0.002	0.011			0.003
C_3H_6						
H_2S	1.293	1.587	1.927	1.644	1.402	1.894
i-C_4H_{10}	0.065	0.015	0.069			0.052
n-C_4H_{10}	0.668	0.771	1.072	0.462	0.433	0.814
1-C_4H_8				0.075	0.030	0.003
i-C_4H_8				0.123	0.045	0.010
t-C_4H_8				0.067	0.030	0.005
c-C_3H_8						
C_2H_6			0.048			
N_2	0.058	0.037	0.018	0.040	0.031	0.055
CH_4	0.012					
Liquid Analysis (wt % of feed)						
Thiophene	0.00	0.00	0.00	0.81	0.50	0.00
Cyclohexane	32.26	36.17	26.45	28.32	30.84	26.42
Cyclohexene	0.00	0.00	0.01	7.54	6.80	0.14
Isoctene	0.00	0.00	0.00	0.54	1.03	0.02
Toluene	24.06	29.70	21.51	26.46	28.88	21.50
Napthalene	0.23	0.57	0.83	5.55	6.16	0.95
Quinoline	0.00	0.24	0.05	0.41	0.77	0.46
Conversion (wt %)						
Thiophene	100.00	100.00	100.00	92.02	95.01	100.00
Cyclohexane	-24.36	-39.44	-1.96	-9.18	-18.87	-1.86
Cyclohexene	100.00	100.00	99.89	43.57	49.12	98.93
Icoctene	100.00	100.00	100.00	94.60	89.74	99.79
Toluene	19.21	0.27	27.78	11.16	3.01	27.82
Naphthalene	96.82	92.08	88.46	22.52	13.97	86.77
Quinoline	100.00	93.43	98.59	88.72	78.70	87.41

TABLE 5. HDS-20 Catalyst, Physical Mixing at Ambient Conditions using 23% Asphaltene Concentration

Exp No.	8701EA	8701EB	8701EC	8701ED	8701EE	87C1EF
Impregnation Conditions	Solvent: Dekalin Temperature: 22°C		Asphaltene Content: 23 wt % Pressure: atm.			
Hydrotreating						
Temp (°C)	400	350	300	400	300	350
Press (MPa)	6.9	5.2	6.9	3.4	3.4	5.2
Yield Summary						
Liquid (wt % feed)	89.7	92.5	87.1	80.8	70.8	93.2
Gas (wt % feed)	3.3	3.9	7.5	5.4	5.0	3.8
H_2 Consumption	0.0104	0.0091	0.0069	0.0084	0.0037	0.0088
Sulphur Conv %	43.3	54.6	66.1	67.9	72.9	48.3
Gas Analysis						
H_2	97.766	97.265	97.437	96.450	97.027	97.532
C_3H_8	0.007	0.003		0.017		0.006
C_3H_6						
H_2S	1.442	1.888	1.887	2.253	2.093	1.579
$i\text{-}C_4H_{10}$	0.069	0.012	0.016	0.087	0.005	0.073
$n\text{-}C_4H_{10}$	0.670	0.801	0.587	1.120	0.591	0.762
$1\text{-}C_4H_8$			0.011		0.079	0.006
$i\text{-}C_4H_8$			0.026		0.107	0.014
$t\text{-}C_4H_8$			0.016		0.079	0.009
$c\text{-}C_3H_8$						
C_2H_4				0.014		
N_2	0.025	0.003	0.02	0.028	0.018	0.019
CH_4	0.021			0.032		
Liquid Analysis (wt % of feed)						
Thiophene	0.00	0.00	0.06	0.00	0.52	0.01
Cyclohexane	33.31	35.64	32.86	29.02	24.02	35.47
Cyclohexene	0.00	0.00	0.66	0.02	6.44	0.28
Isoctene	0.00	0.00	0.17	0.00	0.80	0.07
Toluene	24.39	28.46	27.17	23.07	23.00	28.59
Napthalene	0.16	0.22	0.79	0.62	0.79	0.35
Quinoline	0.00	0.10	0.28	0.03	0.15	0.21
Conversion (wt %)						
Thiophene	100.00	100.00	99.39	100.00	94.77	99.91
Cyclohexane	28.28	-37.24	-26.54	-11.73	7.50	-36.59
Cyclohexene	100.00	100.00	95.06	99.88	51.96	97.91
Isoctene	100.00	100.00	98.26	100.00	92.02	99.26
Toluene	18.57	4.97	9.29	22.98	23.20	4.53
Naphthalene	97.70	96.83	88.69	91.12	88.69	94.95
Quinoline	100.00	97.19	92.30	99.11	95.89	94.08

TABLE 6. HDS-20 Catalyst, Physical Mixing at Ambient Conditions with Tetralin as the Solvent

Exp No.	8701FA	8701FB	8701FC	8701FD	8701FE	8701FF
Impregnation Conditions	Solvent: Tetralin Temperature: 22°C			Pressure: atm		
Hydrotreating						
Temp (°C)	400	350	300	400	300	350
Press (MPa)	6.9	5.2	6.9	3.4	3.4	5.2
Yield Summary						
Liquid (wt % feed)	88.6	68.4	92.2	104.1	58.6	88.5
Gas (wt % feed)	3.6	4.4	4.0	6.5	5.0	5.1
H_2 Consumption	0.0100	0.0117	0.0066	0.0082	0.0067	0.0074
Sulphur Conv %	47.4	60.8	61.2	72.6	67.7	68.3
Gas Analysis						
H_2	97.596	97.121	97.517	95.808	96.665	96.830
C_3H_8	0.009	0.003		0.014		
C_3H_6						
H_2S	1.554	1.978	1.808	2.433	2.139	2.085
$i\text{-}C_4H_{10}$	0.085	0.018		0.084		0.019
$n\text{-}C_4H_{10}$	0.688	0.844	0.634	1.599	0.767	0.988
$1\text{-}C_4H_8$					0.024	
$i\text{-}C_4H_8$					0.070	
$t\text{-}C_4H_8$					0.044	
$c\text{-}C_3H_8$						
C_2H_6	0.009			0.011		
N_2	0.039	0.037	0.041	0.028	0.292	0.078
CH_4				0.024		
Liquid Analysis (wt % of feed)						
Thiophene	0.00	0.00	0.00	0.00	0.18	0.01
Cyclohexane	34.12	23.06	38.67	37.34	20.61	24.04
Cyclohexene	0.00	0.00	0.17	0.02	2.44	0.00
Isoctene	0.00	0.00	0.01	0.00	0.09	0.00
Toluene	25.14	18.31	31.33	23.60	17.43	24.24
Napthalene	0.34	0.26	5.70	1.34	3.88	0.91
Quinoline	0.00	0.12	0.85	0.07	0.32	0.42
Conversion (wt %)						
Thiophene	100.00	100.00	100.00	100.00	98.20	100.00
Cyclohexane	-31.30	11.30	-48.80	-43.70	20.70	7.50
Cyclohexene	100.00	100.00	98.80	99.80	81.80	100.00
Isoctene	100.00	100.00	99.90	100.00	99.10	100.00
Toluene	15.50	38.40	-5.30	20.60	41.40	18.50
Naphthalene	95.20	96.30	18.60	80.80	44.60	87.00
Quinoline	100.00	96.80	76.40	98.00	91.20	88.40

TABLE 7A. HDS-20 Catalyst, Physical Mixing at Ambient Conditions with Cyclohexane as the Solvent

Exp No.	8701GA	8701GB	8701GC	8701GD
Impregnation Conditions	Solvent: Cyclohexane Temperature: 22°C		Pressure: atm.	
Hydrotreating				
Temp (°C)	400	350	300	300
Press (MPa)	6.9	5.2	6.9	3.4
Yield Summary				
Liquid (wt % feed)	88.8	93.2	92.4	94.1
Gas (wt % feed)	3.5	4.2	4.0	5.8
H_2 Consumption	0.0082	0.0104	0.0068	0.0055
Sulphur Conv %	45.9	57.2	61.6	85.1
Gas Analysis				
H_2	97.762	97.243	97.468	96.367
C_3H_8	0.006	0.003		
C_3H_6				
H_2S	1.437	1.855	1.853	2.580
$i\text{-}C_4H_{10}$	0.128	0.016	0.004	
$n\text{-}C_4H_{10}$	0.599	0.861	0.643	0.874
$1\text{-}C_4H_8$				0.025
$i\text{-}C_4H_8$				0.079
$t\text{-}C_4H_8$				0.047
$c\text{-}C_3H_8$				
C_2H_6	0.005			
N_2	0.044	0.022	0.031	0.027
CH_4	0.018			
Liquid Analysis (wt % of feed)				
Thiophene	0.00	0.00	0.00	0.16
Cyclohexane	36.04	37.38	36.41	36.70
Cyclohexene	0.00	0.00	0.06	1.39
Isoctene	0.00	0.00	0.00	0.12
Toluene	25.74	28.96	28.32	30.13
Naphthalene	0.14	0.33	4.78	6.37
Quinoline	0.02	0.09	0.85	0.68
Conversion (wt %)				
Thiophene	100.00	100.00	100.00	98.40
Cyclohexane	-38.70	-43.80	-40.10	-41.20
Cyclohexene	100.00	100.00	99.50	89.60
Isoctene	100.00	100.00	100.00	98.80
Toluene	13.40	2.60	4.80	-1.30
Naphthalene	98.00	95.30	31.80	9.00
Quinoline	99.5	97.40	76.40	81.20

TABLE 7B. HDS-20 Catalyst, Physical Mixing at Ambient Conditions with Cyclohexane as the Solvent

Exp No.	8701GE	8701GF	8701GG	8701GH
Impregnation Conditions	Solvent: Cyclohexane Temperature: 22°C		Pressure: atm.	
Hydrotreating				
Temp (°C)	250	350	250	300
Press (MPa)	5.2	1.7	1.7	3.4
Yield Summary				
Liquid (wt % feed)	97.5	88.6	97.1	95.2
Gas (wt % feed)	1.7	8.0	1.6	5.8
H_2 Consumption	0.0015	0.0060	0.0004	0.0054
Sulphur Conv %	23.9	97.6	13.8	80.5
Gas Analysis				
H_2	99.034	95.031	99.151	96.573
C_3H_8		0.005		0.004
C_3H_6				
H_2S	0.642	3.083	0.370	2.334
$i\text{-}C_4H_{10}$		0.055		0.009
$n\text{-}C_4H_{10}$	0.180	1.725	0.141	0.875
$1\text{-}C_4H_8$	0.041	0.011	0.073	0.030
$i\text{-}C_4H_8$	0.036	0.031	0.065	0.092
$t\text{-}C_4H_8$	0.030	0.020	0.058	0.055
$c\text{-}C_3H_8$				
C_2H_6				
N_2	0.037	0.038	0.143	0.027
CH_4				
Liquid Analysis (wt % of feed)				
Thiophene	3.19	0.00	7.52	0.12
Cyclohexane	31.92	32.03	27.76	31.69
Cyclohexene	13.11	0.35	11.81	1.21
Isoctene	7.35	0.00	6.81	0.13
Toluene	31.86	26.79	30.39	26.26
Napthalene	7.38	4.98	7.34	5.03
Quinoline	0.13	0.66	0.06	0.50
Conversion (wt %)				
Thiophene	68.00	100.00	24.80	98.80
Cyclohexane	-22.80	-23.20	-6.70	-21.80
Cyclohexene	1.80	97.30	11.80	91.00
Isoctene	28.90	100.00	31.70	98.70
Toluene	-7.10	9.90	-1.70	12.20
Naphtahalene	-5.40	28.90	-3.00	29.50
Quinoline	96.50	81.50	98.40	86.30

TABLE 8. HDS-20 Catalyst, Physical Mixing at Ambient Conditions with Toluene as the Solvent

Exp No.	8701HA	8701HB	8701HC	8701HD	8701HE	8701HF
Impregnation Conditions	Solvent: Toluene Temperature: 22°C			Pressure: atm		
Hydrotreating						
Temp (°C)	350	300	250	350	250	300
Press (MPa)	5.2	3.4	5.2	1.7	1.7	3.4
Yield Summary						
Liquid (wt % feed)	92.4	92.0	91.8	89.4	93.8	90.3
Gas (wt % feed)	4.4	5.8	1.5	7.8	1.4	5.5
H_2 Consumption	0.0075	0.0047	0.0002	0.0059	-0.0015	0.0053
Sulphur Conv %	56.1	83.4	18.6	98.2	12.4	77.1
Gas Analysis						
H_2	97.346	96.666	99.259	95.429	99.308	96.891
C_3H_8	0.006	0.004	0.002	0.008	0.002	0.004
C_3H_6						
H_2S	1.720	2.330	0.468	2.924	0.316	2.118
$i\text{-}C_4H_{10}$	0.014			0.035		0.006
$n\text{-}C_4H_{10}$	0.794	0.778	0.148	1.539	0.133	0.789
$1\text{-}C_4H_8$		0.037	0.035	0.003	0.075	0.025
$i\text{-}C_4H_8$		0.088	0.032	0.015	0.065	0.073
$t\text{-}C_4H_8$		0.051	0.024	0.011	0.058	0.044
$c\text{-}C_3H_8$						
C_2H_6						
N_2	0.120	0.043	0.034	0.033	0.043	0.051
CH_4				0.004		
Liquid Analysis (wt % of feed)						
Thiophene	0.00	0.34	3.41	0.03	7.06	0.15
Cyclohexane	34.21	29.82	23.65	31.80	29.02	32.66
Cyclohexene	0.00	4.53	9.93	0.27	13.29	1.35
Isoctene	0.00	0.27	4.98	0.00	6.74	0.18
Toluene	26.75	26.10	24.13	26.90	31.80	27.87
Napthalene	0.16	5.23	5.87	5.27	7.79	6.05
Quinoline	0.03	0.70	0.23	0.70	0.09	0.69
Conversion (wt %)						
Thiophene	100.00	96.60	65.80	99.70	29.30	98.50
Cyclohexane	-31.50	-14.60	9.10	-22.20	-11.50	-25.50
Cyclohexene	100.00	66.20	25.80	98.00	0.70	90.00
Isoctene	100.00	97.30	50.00	100.00	32.40	98.20
Toluene	10.50	12.70	19.30	10.00	-6.40	6.80
Naphthalene	97.80	26.70	17.70	26.10	-9.20	15.10
Quinoline	99.20	80.60	93.60	80.70	97.40	81.00

TABLE 9. HDS-20 Catalyst, Physical Mixing at 200°C, 4.1 MPa

Exp No.	8702IA	8702IB	8702IC	8702ID	8702IE	8702IF
Impregnation Conditions	Solvent: Dekalin		Asphaltene Content: 9 wt %			
	Temperature: 200°C		Pressure: 4.1 MPa			
Hydrotreating						
Temp (°C)	350	300	250	350	250	300
Press (MPa)	5.2	3.4	5.2	1.7	1.7	3.4
Yield Summary						
Liquid (wt % feed)	80.7	88.5	94.3	92.5	93.6	93.7
Gas (wt % feed)	4.3	4.6	1.2	7.8	0.6	4.2
H_2 Consumption	0.0069	0.0019	-0.0008	0.0046	-0.0008	0.0036
Sulphur Conv %	59.0	62.9	13.1	95.4	2.4	54.4
Gas Analysis						
H_2	97.350	97.300	99.371	95.299	99.684	97.617
C_2H_6	0.005	0.004	0.002	0.009	0.024	0.004
C_3H_6						
H_2S	1.759	1.755	0.335	2.896	0.067	1.537
$i\text{-}C_4H_{10}$	0.009	0.008		0.095		0.004
$n\text{-}C_4H_{10}$	0.739	0.475	0.132	1.439	0.056	0.495
$1\text{-}C_4H_8$		0.076	0.033	0.043	0.048	0.077
$i\text{-}C_4H_8$		0.103	0.027	0.091	0.026	0.127
$t\text{-}C_4H_8$		0.075	0.022	0.063	0.026	0.091
$c\text{-}C_3H_8$						
C_2H_4				0.011		
N_2	0.139	0.205	0.077	0.048	0.069	0.050
CH_4				0.006		
Liquid Analysis (wt % of feed)						
Thiophene	0.00	0.00	0.06	0.00	0.52	0.01
Cyclohexane	33.31	35.64	32.86	29.02	24.02	35.47
Cyclohexene	0.00	0.00	0.66	0.02	6.44	0.28
Isoctene	0.00	0.00	0.17	0.00	0.80	0.07
Toluene	24.39	28.46	27.17	23.07	23.00	28.59
Napthalene	0.16	0.22	0.79	0.62	0.79	0.35
Quinoline	0.00	0.10	0.28	0.03	0.15	0.21
Conversion (wt %)						
Thiophene	100.00	100.00	99.39	100.00	94.77	99.91
Cyclohexane	-28.28	-37.24	-26.54	-1.73	7.50	-36.59
Cyclohexene	100.00	100.00	95.06	99.88	51.96	97.91
Isoctene	100.00	100.00	98.26	100.00	92.02	99.26
Toluene	18.57	4.97	9.29	22.98	23.20	4.53
Naphthalene	97.70	96.83	88.69	91.12	88.69	94.95
Quinoline	100.00	97.19	92.30	99.11	95.89	94.08

TABLE 10. HDS-20 Catalyst, Physical Mixing at 200°C, 6.2 MPa

Exp No.	8701JA	8701JB	8701JC	8701JD	8701JE	8701JF
Impregnation Conditions	Solvent: Dekalin		Asphaltene Content: 9 wt %			
	Temperature: 200°C		Pressure: 6.2 MPa			
Hydrotreating						
Temp (°C)	400	350	300	400	300	350
Press (MPa)	6.9	5.2	6.9	3.4	3.4	5.2
Yield Summary						
Liquid (wt % feed)	72.7	79.4	81.0	95.8	84.1	77.1
Gas (wt % feed)	6.6	10.9	11.7	12.8	13.1	11.7
H_2 Consumption	0.0192	0 0182	0.0187	0.0182	0.0182	0.0204
Sulphur Conv %	57.7	88 2	104.3	105.6	109.5	100.5
Gas Analysis						
H_2	95.020	91.550	91.800	90.000	90.590	91.560
C_3H_8	0.020	0.020	0.010	0.080	0.010	0.010
C_3H_6						
H_2S	2.370	3.750	4.050	4.620	4.390	4.050
i-C_4H_{10}	0.200	0.160	0.110	0.370	0.130	0.180
n-C_4H_{10}	2.270	4.020	3.940	4.710	4.630	4.100
1-C_4H_8						
i-C_4H_8						
t-C_4H_8					0.010	
c-C_3H_8						
C_2H_6	0.010	0.010		0.040		0.010
N_2	0.040	0.480	0.090	0.080	0.240	0.020
CH_4		0.020		0.100		0.080
Liquid Analysis (wt % of feed)						
Thiophene	0.00	0.00	0.01	1.04	0.09	0.00
Cyclohexane	28.03	24.42	29.88	35.68	36.58	34.18
Cyclohexene	0.00	0.01	0.02	0.06	0.03	0.02
Isoctene	0.00	0.00	0.00	0.00	0.00	0.00
Toluene	21.37	20.33	25.65	30.93	30.92	28.58
Napthalene	0.17	0.16	0.72	1.22	5.22	0.30
Quinoline	0.00	0.03	0.49	0.07	0.89	0.15
Conversion (wt %)						
Thiophene	100.00	100.00	99.92	89.69	99.09	100.00
Cyclohexane	-7.90	6.02	-15.02	-37.32	-40.81	-31.56
Cyclohexene	100.00	99.94	99.82	99.57	99.75	99.89
Isoctene	100.00	100.00	100.00	100.00	100.00	100.00
Toluene	99.42	32.04	14.23	-3.42	-3.39	4.44
Naphthalene	97.53	97.74	89.75	82.69	25.71	95.72
Quinoline	100.00	99.12	86.57	98.15	75.37	95.74

TABLE 11. HDS-20 Catalyst, Physical Mixing at 300°C and 4.2 MPa

Exp No.	8701KA	8701KB	8701KC	8701KD	8701KE	8701KF
Impregnation Conditions	Solvent: Dekalin		Asphaltene Content: 9 wt %			
	Temperature: 300°C		Pressure: 4.2 MPa			
Hydrotreating						
Temp (°C)	400	350	300	400	300	350
Press (MPa)	6.9	5.2	6.9	3.4	3.4	5.2
Yield Summary						
Liquid (wt % feed)	111.0	99.1	95.4	107.2	89.3	94.6
Gas (wt % feed)	6.7	8.1	6.3	12.0	6.7	3.8
H_2 Consumption	0.0034	-0.0007	0.0070	0.0572	0.0078	0.0206
Sulphur Conv %	51.5	77.0	73.9	100.8	62.4	50.4
Gas Analysis						
H_2	96.800	97.000	97.350	97.620	95.570	96.280
C_3H_8	0.010			0.010		
C_3H_6						
H_2S	1.390	1.530	1.600	1.110	2.210	2.450
$i\text{-}C_4H_{10}$	0.060	0.020	0.010	0.050	0.020	0.050
$n\text{-}C_4H_{10}$	1.620	1.370	0.910	1.190	1.520	1.170
$1\text{-}C_4H_8$			0.020		0.140	
$i\text{-}C_4H_8$						
$t\text{-}C_4H_8$			0.040		0.280	
$c\text{-}C_3H_8$			0.030		0.170	
C_2H_6						
N_2	0.090	0.070	0.040	0.020	0.090	0.070
CH_4	0.010					0.010
Liquid Analysis (wt % of feed)						
Thiophene	0.00	0.00	0.10	0.00	0.58	0.00
Cyclohexane	41.17	32.66	32.92	37.93	28.15	36.51
Cyclohexene	0.00	0.02	0.96	0.01	7.18	0.02
Isoctene	0.00	0.00	0.39	0.00	0.88	0.00
Toluene	30.38	30.53	28.36	34.38	26.76	28.24
Napthalene	0.22	0.55	1.30	1.26	6.53	1.08
Quinoline	0.00	0.36	0.62	0.08	0.60	0.61
Conversion (wt %)						
Thiophene	100.00	100.00	99.05	100.00	94.21	100.00
Cyclohexane	-59.26	-25.48	-26.48	-45.71	-8.13	-40.25
Cyclohexene	100.00	99.85	92.80	99.92	46.34	99.86
Isoctene	100.00	100.00	96.07	100.00	91.12	100.00
Toluene	-1.57	-2.25	5.02	-15.13	10.37	5.43
Naphthalene	96.84	92.11	81.54	82.01	7.14	84.66
Quinoline	100.00	90.41	83.33	97.98	83.92	83.47

TABLE 12. HDS-20 Catalyst, Physical Mixing at 300°C and 8.3 MPa

Exp No.	8701LA	8701LB	8701LC	8701LD	8701LE	8701LF
Impregnation Conditions	Solvent: Dekalin			Asphaltene Content: 9 wt %		
	Temperature: 300°C			Pressure: 8.3 MPa		
Hydrotreating						
Temp (°C)	350	300	250	350	250	300
Press (MPa)	5.2	3.4	5.2	1.7	1.7	3.4
Yield Summary						
Liquid (wt % feed)	80.7	84.4	86.4	118.0	92.2	93.4
Gas (wt % feed)	4.1	5.7	2.0	8.0	1.4	3.9
H_2 Consumption	0.0079	0.0050	0.0010	0.0059	-0.0002	0.0032
Sulphur Conv %	56.7	80.8	22.6	100.5	15.1	53.1
Gas Analysis						
H_2	97.366	96.452	98.945	95.543	99.258	97.743
C_3H_8	0.006	0.055	0.002	0.009	0.001	0.004
C_3H_6						
H_2S	1.753	2.406	0.597	2.853	0.398	1.503
i-C_4H_{10}	0.008			0.037		
n-C_4H_{10}	0.773	0.933	0.253	1.510	0.119	0.452
1-C_4H_8		0.013	0.040	0.003	0.076	0.080
i-C_4H_8		0.048	0.048	0.007	0.056	0.102
t-C_4H_8		0.021	0.037	0.005	0.052	0.075
c-C_3H_8						
C_2H_6				0.005		
N_2	0.094	0.071	0.079	0.047	0.040	0.041
CH_4						
Liquid Analysis (wt % of feed)						
Thiophene	0.00	0.12	1.60	0.19	7.45	1.27
Cyclohexane	35.95	30.38	28.48	45.17	27.87	31.58
Cyclohexene	0.00	0.79	11.22	0.61	12.70	11.30
Isoctene	0.00	0.14	5.90	0.12	7.87	2.00
Toluene	27.84	24.83	28.46	38.15	31.93	30.96
Napthalene	0.18	4.67	6.29	7.21	7.56	6.96
Quinoline	0.05	0.81	0.18	0.93	0.08	0.72
Conversion (wt %)						
Thiophene	100.00	98.81	83.85	98.10	25.35	87.27
Cyclohexane	-39.56	-17.92	-10.55	-74.29	-7.37	-21.64
Cyclohexene	100.00	94.05	15.87	95.40	4.90	15.35
Isoctene	100.00	98.72	44.17	98.85	21.18	79.99
Toluene	6.45	16.56	4.37	-27.80	-6.68	-3.45
Naphthalene	97.45	32.94	9.63	-2.85	-7.24	1.30
Quinoline	98.69	78.16	95.11	75.01	97.78	80.77

TABLE 13A. Fresh HDS-20 Catalyst

Exp No.	HDS20FA	HDS20FB	HDS20FC	HDS20FD	HDS20FE
Impregnation Conditions	Fresh American Cyanamid HDS-20				
Hydrotreating					
Temp (°C)	400	350	300	400	300
Press (MPa)	6.9	5.2	6.9	3.4	3.4
Yield Summary					
Liquid (wt % feed)	84.5	104.1	78.0	80.1	105.9
Gas (wt % feed)	4.1	7.6	4.0	5.0	5.5
H_2 Consumption	0.0098	0.0086	0.0050	0.0084	0.0057
Sulphur Conv %	51.3	79.4	58.8	65.2	81.0
Gas Analysis					
H_2	97.422	95.337	97.488	95.565	96.557
C_3H_8	0.016	0.010	0.004	0.017	0.006
C_3H_6					
H_2S	1.578	2.562	1.712	2.192	2.428
i-C_4H_{10}	0.111	0.039	0.006	0.075	
n-C_4H_{10}	0.675	1.926	0.543	1.002	0.786
1-C_4H_8			0.008		0.026
i-C_4H_8			0.023		0.074
t-C_4H_8			0.012		0.044
c-C_3H_8					
C_2H_6	0.013			0.011	
N_2	0.168	0.126	0.204	0.116	0.079
CH_4	0.018			0.022	
Liquid Analysis (wt % of feed)					
Thiophene	0.00	0.00	0.15	0.00	0.24
Cyclohexane	31.21	35.86	27.63	29.90	36.94
Cyclohexene	0.00	0.00	0.96	0.00	1.57
Isoctene	0.00	0.00	0.30	0.00	0.11
Toluene	22.02	27.94	22.89	23.54	31.27
Napthalene	0.08	0.18	1.37	0.69	6.20
Quinoline	0.00	0.01	0.42	0.01	0.55
Conversion (wt %)					
Thiophene	100.00	100.00	98.50	100.00	97.50
Cyclohexane	-20.70	38.60	-6.60	-15.40	-42.50
Cyclohexene	100.00	100.00	92.90	100.00	88.30
Isoctene	100.00	100.00	97.00	100.00	99.00
Toluene	26.40	6.60	23.30	21.10	-4.90
Naphthalene	98.80	97.50	80.40	90.10	11.40
Quinoline	100.00	99.70	88.40	99.80	84.80

TABLE 13B. Fresh HDS-20 Catalyst

Exp No.	HDS20FF	HDS20FG	HDS20FH	HDS20FI	HDS20FJ
Impregnation Conditions	Fresh American Cyanamid HDS-20				
Hydrotreating					
Temp (°C)	350	250	350	250	300
Press (MPa)	5.2	5.2	1.7	1.7	3.4
Yield Summary					
Liquid (wt % feed)	94.1	93.1	91.6	94.9	92.1
Gas (wt % feed)	4.1	2.2	7.2	1.3	5.4
H_2 Consumption	0.0087	0.0020	0.0045	-0.0004	0.0051
Sulphur Conv %	59.8	34.0	90.0	14.2	76.5
Gas Analysis					
H_2	97.289	98.697	95.585	99.312	96.786
C_3H_8	0.006	0.003		0.002	0.005
C_3H_6					
H_2S	1.881	0.932	2.791	0.372	2.219
i-C_4H_{10}	0.014	0.176	0.073	0.014	0.014
n-C_4H_{10}	0.719	0.040	1.325	0.094	0.707
1-C_4H_8		0.035	0.026	0.067	0.035
i-C_4H_8		0.028	0.066	0.046	0.094
t-C_4H_8			0.042	0.043	0.058
c-C_3H_8					
C_2H_6					
N_2	0.090	0.090	0.092	0.0[illegible]4	0.082
CH_4					
Liquid Analysis (wt % of feed)					
Thiophene	0.00	4.15	0.24	7.04	0.29
Cyclohexane	34.05	26.96	32.30	24.18	30.18
Cyclohexene	0.03	12.28	1.06	11.10	4.74
Isoctene	0.00	6.44	0.16	7.02	8.23
Toluene	26.55	28.37	27.83	28.21	26.55
Napthalene	0.56	6.00	5.86	6.86	5.54
Quinoline	0.24	0.11	0.60	0.06	0.41
Conversion (wt %)					
Thiophene	100.00	58.20	97.60	29.10	97.00
Cyclohexane	-31.40	-4.00	-24.60	6.70	-16.40
Cyclohexene	99.80	8.70	92.10	17.40	64.70
Isoctene	100.00	37.20	98.40	31.60	19.70
Toluene	11.00	4.90	6.70	5.40	11.00
Naphthalene	91.90	14.20	16.10	1.80	20.70
Quinoline	93.50	96.90	83.30	98.40	88.60
Sulphur	59.80	34.00	90.00	14.20	76.50

TABLE 14. Deactivated HDS-20 Catalyst

Exp No.	HDS20DA	HDS20DB	HDS20DC	HDS20DD	HDS20DE	HDS20DF
Impregnation Conditions	Deactivated HDS-20 supplied by SRC					
Hydrotreating						
Temp (°C)	350	300	250	350	250	300
Press (MPa)	5.2	3.4	5.2	1.7	1.7	3.4
Yield Summary						
Liquid (wt % feed)	88.4	91.6	87.6	90.4	90.0	97.8
Gas (wt % feed)	4.8	2.5	0.9	7.3	0.7	1.2
H_2 Consumption	0.0061	0.0013	-0.0004	0.0037	-0.0021	-0.0004
Sulphur Conv %	69.2	31.3	9.5	91.2	4.3	24.7
Gas Analysis						
H_2	97.050	98.556	99.465	95.905	99.638	98.932
C_3H_8	0.013			0.007		0.001
C_3H_6						
H_2S	2.039	0.861	0.249	2.557	0.112	0.626
$i\text{-}C_4H_{10}$	0.076	0.003		0.087		
$n\text{-}C_4H_{10}$	0.679	0.247	0.072	0.995	0.036	0.178
$1\text{-}C_4H_8$	0.008	0.052	0.030	0.063	0.037	0.051
$i\text{-}C_4H_8$	0.017	0.062	0.023	0.165	0.022	0.056
$t\text{-}C_4H_8$	0.011	0.043	0.020	0.113	0.020	0.044
$c\text{-}C_3H_8$						
C_2H_6						
N_2	0.108	0.176	0.141	0.106	0.136	0.114
CH_4						
Liquid Analysis (wt % of feed)						
Thiophene	0.17	6.09	6.73	0.54	9.77	7.68
Cyclohexane	33.90	30.63	27.87	34.38	28.62	32.86
Cyclohexene	0.92	15.08	12.39	7.96	13.99	14.33
Isoctene	0.45	8.15	8.82	0.75	11.33	9.81
Toluene	27.50	31.98	30.18	32.21	33.31	36.00
Napthalene	4.46	7.57	7.23	7.07	8.71	9.53
Quinoline	0.78	0.57	0.08	0.51	0.06	0.67
Conversion (wt %)						
Thiophene	98.30	38.80	32.50	94.60	2.00	22.90
Cyclohexane	-30.20	-17.70	-7.10	-32.10	-10.00	-26.20
Cyclohexene	93.20	-12.30	7.80	40.80	-4.20	-6.70
Isoctene	95.50	18.60	11.90	92.50	-13.20	2.00
Toluene	8.10	-6.80	-0.80	-7.60	-11.30	-20.30
Naphthalene	36.50	-7.80	-2.90	-0.70	-24.01	-35.70
Quinoline	78.50	84.30	97.80	86.00	98.30	81.60

TABLE 15. Fresh Harshaw Catalyst

Exp No.	HARFA	HARFB	HARFC	HARFD	HARFE	HARFF
Impregnation Conditions	Harshaw Fresh Catalyst					
Hydrotreating						
Temp (°C)	350	300	250	350	250	300
Press (MPa)	5.2	3.4	5.2	1.7	1.7	3.4
Yield Summary						
Liquid (wt % feed)	90.3	90.0	95.6	87.7	91.9	94.5
Gas (wt % feed)	4.4	5.3	1.2	7.6	1.1	4.9
H_2 Consumption	0.0085	0.0047	0.0047	0.0053	-0.0001	0.0046
Sulphur Conv %	61.3	76.6	15.1	85.2	12.4	69.4
Gas Analysis						
H_2	97.174	96.760	99.301	95.339	99.417	97.177
C_3H_8	0.007	0.007		0.009	0.004	0.006
C_3H_6						
H_2S	1.892	2.235	0.425	2.746	0.340	1.959
i-C_4H_{10}	0.020			0.068		
n-C_4H_{10}	0.793	0.649	0.138	1.490	0.104	0.637
1-C_4H_8		0.041	0.031	0.024	0.048	0.043
i-C_4H_8		0.086	0.024	0.048	0.034	0.086
t-C_4H_8		0.057	0.019	0.030	0.021	0.057
c-C_3H_8						
C_2H_6				0.006		
N_2	0.115	0.167	0.062	0.239	0.032	0.036
CH_4						
Liquid Analysis (wt % of feed)						
Thiophene	0.00	0.80	5.85	0.34	8.83	0.98
Cyclohexane	34.13	29.61	31.25	23.43	31.54	36.51
Cyclohexene	0.00	6.21	13.14	0.93	13.52	7.77
Isoctene	0.00	0.44	7.71	0.22	7.89	0.00
Toluene	26.79	26.94	32.85	20.63	33.41	32.79
Napthalene	0.24	5.96	7.77	3.95	8.24	7.41
Quinoline	0.04	0.50	0.10	0.53	0.06	0.59
Conversion (wt %)						
Thiophene	100.00	92.00	41.30	96.60	11.30	90.10
Cyclohexane	-31.10	-13.80	-20.10	10.00	-21.20	-40.20
Cyclohexene	100.00	53.80	2.20	93.10	-0.70	42.60
Isoctene	100.00	95.60	23.00	97.80	21.10	100.00
Toluene	10.50	10.00	-9.70	31.10	-11.60	-9.90
Naphthalene	96.50	15.10	-10.70	43.80	-17.40	-4.90
Quinoline	99.00	86.30	97.40	85.40	98.20	83.90

TABLE 16. Harshaw Catalyst, Asphaltene Impregnation by Physical Mixing at 200°C, 7.2 MPa

Exp No.	HAR1A	HAR1B	HAR1C	HAR1D	HAR1E	HAR1F
Impregnation Conditions	Solvent: Dekalin Temperature: 200°C			Asphaltene Content: 9 wt % Pressure: 7.2 MPa		
Hydrotreating						
Temp (°C)	350	300	250	350	250	300
Press (MPa)	5.2	3.4	5.2	1.7	1.7	3.4
Yield Summary						
Liquid (wt % feed)	91.8	91.6	97.0	84.4	93.8	89.4
Gas (wt % feed)	4.5	5.7	1.4	6.5	1.5	5.2
H_2 Consumption	0.0083	0.0054	0.0013	0.0036	-0.0022	0.0059
Sulphur Conv %	64.5	84.4	18.4	89.2	16.1	76.1
Gas Analysis						
H_2	97.491	96.513	99.189	95.953	99.250	96.983
C_2H_6	0.006	0.005	0.003	0.007	0.005	0.005
C_3H_6						
H_2S	1.745	2.474	0.495	2.711	0.412	2.108
i-C_4H_{10}				0.015		
n-C_4H_{10}	0.685	0.850	0.151		0.122	0.006
1-C_4H_8		0.018	0.027	1.129	0.053	0.759
i-C_4H_8		0.043	0.024	0.018	0.048	0.019
t-C_4H_8		0.026	0.019	0.036	0.039	0.046
c-C_3H_8				0.023		0.028
C_2H_4						
N_2	0.074	0.017	0.092	0.107	0.072	0.046
CH_4						
Liquid Analysis (wt % of feed)						
Thiophene	0.00	0.42	4.17	0.49	5.70	0.38
Cyclohexane	38.79	33.76	22.02	34.38	19.68	39.11
Cyclohexene	0.00	1.39	9.56	1.26	9.49	1.53
Isoctene	0.00	0.16	5.07	0.36	4.93	0.29
Toluene	30.91	29.54	23.20	29.68	22.15	32.57
Napthalene	0.36	6.53	5.34	5.84	5.34	7.20
Quinoline	0.15	0.71	0.09	0.82	0.13	0.77
Conversion (wt %)						
Thiophene	100.00	95.80	58.30	95.10	43.00	96.20
Cyclohexane	-49.60	-30.20	15.10	-32.50	24.10	-50.80
Cyclohexene	100.00	89.70	29.30	90.70	29.80	88.70
Isoctene	100.00	98.40	49.10	96.40	50.50	97.10
Toluene	-3.50	1.00	22.30	0.60	25.80	-9.10
Naphthalene	94.90	7.50	24.30	17.30	24.40	-1.90
Quinoline	96.00	80.40	97.60	77.50	96.40	78.90

TABLE 17. Harshaw Catalyst, Physical Mixing at 200°C

Exp No.	HAR2A	HAR2B	HAR2C	HAR2D	HAR2E	HAR2F
Impregnation Conditions	Solvent: Dekalin Temperature: 200°C			Asphaltene Content: 9 wt % Pressure: atm		
Hydrotreating						
Temp (°C)	350	300	250	350	250	300
Press (MPa)	5.2	3.4	5.2	1.7	1.7	3.4
Yield Summary						
Liquid (wt % feed)	84.9	90.3	90.4	89.4	92.5	94.1
Gas (wt % feed)	3.7	4.8	1.2	6.3	1.3	3.3
H_2 Consumption	0.0103	0.0057	0.0034	0.0063	0.0002	0.0053
Sulphur Conv %	54.6	70.2	14.6	81.5	13.3	52.7
Gas Analysis						
H_2	97.447	96.945	99.299	96.051	99.278	97.901
C_3H_8	0.006	0.005	0.001	0.009	0.007	0.008
C_3H_6						
H_2S	1.804	2.127	0.414	2.531	0.358	1.544
i-C_4H_{10}				0.022		
n-C_4H_{10}	0.662	0.699	0.123	1.153	0.114	0.299
1-C_4H_8		0.020	0.025	0.022	0.044	0.034
i-C_4H_8		0.040	0.022	0.047	0.041	0.055
t-C_4H_8		0.026	0.018	0.032	0.036	0.037
c-C_3H_8						
C_2H_6				0.005		
N_2	0.081	0.138	0.099	0.124	0.123	0.122
CH_4				0.006		
Liquid Analysis (wt % of feed)						
Thiophene	0.03	0.72	4.38	0.32	6.79	0.99
Cyclohexane	39.85	29.83	21.04	31.93	28.59	30.33
Cyclohexene	0.09	4.56	8.88	0.99	10.11	6.39
Isoctene	0.00	0.43	5.30	0.15	3.02	0.70
Toluene	31.50	26.31	22.20	27.73	26.09	27.45
Napthalene	0.72	5.52	5.66	5.39	6.56	6.07
Quinoline	0.31	0.58	0.08	0.68	0.06	0.48
Conversion (wt %)						
Thiophene	99.70	92.80	56.10	96.80	32.00	90.10
Cyclohexane	-53.30	-14.80	19.10	-22.90	-10.00	-16.70
Cyclohexene	99.30	66.00	33.90	92.60	24.70	52.40
Isoctene	100.00	95.70	47.00	98.50	69.80	93.00
Toluene	-5.30	12.20	26.10	7.40	13.00	8.40
Naphthalene	89.70	21.60	19.60	23.40	6.80	13.80
Quinoline	91.60	84.10	97.80	81.30	98.50	86.80

TABLE 18. Harshaw Catalyst, Physical Mixing at 6.9 MPa

Exp No.	HAR3A	HAR3B	HAR3C	HAR3D	HAR3E	HAR3F
Impregnation Conditions	Solvent: Dekalin Temperature: 22°C			Asphaltene Content: 9 wt % Pressure: 6.9 MPa		
Hydrotreating						
Temp (°C)	350	300	250	350	250	300
Press (MPa)	5.2	3.4	5.2	1.7	1.7	3.4
Yield Summary						
Liquid (wt % feed)	69.9	102.0	94.8	86.6	93.5	89.6
Gas (wt % feed)	4.3	5.2	1.4	7.7	1.5	5.3
H_2 Consumption	0.0083	0.0066	0.0017	0.0062	0.0005	0.0056
Sulphur Conv %	59.0	81.7	15.5	98.9	14.7	73.8
Gas Analysis						
H_2	97.176	96.729	99.241	95.168	99.152	96.744
C_3H_8	0.007	0.003		0.004	0.004	0.006
C_3H_6						
H_2S	1.886	2.417	0.400	3.088	0.412	2.196
i-C_4H_{10}	0.037			0.067		0.013
n-C_4H_{10}	0.798	0.645	0.150	1.451	0.134	0.756
1-C_4H_8		0.018	0.030	0.007	0.059	0.031
i-C_4H_8		0.048	0.024	0.031	0.045	0.064
t-C_4H_8		0.025	0.019	0.020	0.040	0.042
c-C_3H_8						
C_2H_6				0.005		
N_2	0.097	0.117	0.137	0.162	0.154	0.150
CH_4						
Liquid Analysis (wt % of feed)						
Thiophene	0.00	0.34	4.81	0.13	6.27	0.36
Cyclohexane	30.85	31.66	24.23	34.25	22.21	29.90
Cyclohexene	0.00	4.09	10.30	0.76	9.92	3.96
Isoctene	0.00	0.30	6.49	0.00	5.97	0.00
Toluene	23.61	27.38	25.77	29.63	25.08	26.31
Napthalene	0.26	1.50	6.18	5.65	3.17	5.55
Quinoline	0.06	0.63	0.14	0.71	0.06	0.59
Conversion (wt %)						
Thiophene	100.00	96.60	51.90	98.70	37.20	96.40
Cyclohexane	-18.70	-21.80	6.80	-31.80	14.60	-15.00
Cyclohexene	100.00	69.50	23.30	94.30	26.20	70.60
Isoctene	100.00	97.00	54.00	100.00	40.30	100.00
Toluene	21.30	8.60	14.10	1.00	16.50	12.40
Naphthalene	96.30	78.70	12.20	19.70	54.60	20.50
Quinoline	98.30	82.60	96.10	80.40	98.40	83.60

TABLE 19. Harshaw Catalyst, Physical Mixing at Ambient Conditions

Exp No.	HAR4A	HAR4B	HAR4C	HAR4D	HAR4E	HAR4F
Impregnation Conditions	Solvent: Dekalin Temperature: 22°C			Asphaltene Content: 9 wt % Pressure: atm		
Hydrotreating						
Temp (°C)	350	300	250	350	250	300
Press (MPa)	5.2	3.4	5.2	1.7	1.7	3.4
Yield Summary						
Liquid (wt % feed)	90.1	88.5	95.6	91.4	90.2	95.9
Gas (wt % feed)	4.0	2.9	1.2	7.2	0.6	2.5
H_2 Consumption	0.0075	0.0027	0.0016	0.0055	-0.0009	0.0009
Sulphur Conv %	56.8	42.5	14.2	92.3	4.6	31.2
Gas Analysis						
H_2	97.590	98.281	99.348	99.562	99.653	98.717
C_3H_8	0.004	0.003		0.009	0.002	0.004
C_3H_6						
H_2S	1.638	1.195	0.372	2.856	0.126	0.825
i-C_4H_{10}				0.029		0.004
n-C_4H_{10}	0.680	0.311	0.118	1.319	0.040	0.261
1-C_4H_8		0.053	0.024	0.032	0.018	0.048
i-C_4H_8		0.049	0.018	0.054	0.012	0.043
t-C_4H_8		0.038	0.015	0.037	0.011	0.043
c-C_3H_8						0.034
C_2H_6				0.005		
N_2	0.088	0.070	0.106	0.098	0.138	0.066
CH_4						
Liquid Analysis (wt % of feed)						
Thiophene	0.05	4.33	5.63	0.33	6.61	5.06
Cyclohexane	34.72	22.66	25.63	32.21	18.58	23.58
Cyclohexene	0.22	9.57	12.65	1.14	9.25	10.92
Isoctene	0.04	0.00	5.69	0.19	6.94	0.00
Toluene	28.09	23.66	26.69	28.18	22.31	25.12
Napthalene	0.31	1.35	5.45	4.95	4.58	5.19
Quinoline	0.09	0.27	0.13	0.70	0.06	0.41
Conversion (wt %)						
Thiophene	99.50	56.70	43.60	96.70	33.80	49.30
Cyclohexane	-33.80	12.70	1.30	-24.10	28.40	9.20
Cyclohexene	98.40	28.90	6.00	91.50	31.20	18.80
Isoctene	99.60	100.00	43.10	98.10	30.60	100.00
Toluene	6.40	21.20	11.10	6.20	25.70	16.40
Naphthalene	95.60	80.70	21.90	29.00	34.40	25.70
Quinoline	97.50	92.60	96.30	80.50	98.20	88.50

TABLE 20. Fresh F145 Catalyst

Exp No.	F145FA	F145FB	F145FC	F145FD	F145FE	F145FF
Impregnation Conditions	Fresh F145 catalyst supplied by CANMET					
Hydrotreating						
Temp (°C)	350	300	250	350	250	300
Press (MPa)	5.2	3.4	5.2	1.7	1.7	3.4
Yield Summary						
Liquid (wt % feed)	87.7	93.6	96.6	111.4	92.5	97.3
Gas (wt % feed)	4.4	3.1	0.4	7.1	0.2	0.8
H_2 Consumption	0.0062	0.0000	-0.0011	0.0033	-0.0025	-0.0023
Sulphur Conv %	57.2	43.2	6.5	83.8	1.0	10.0
Gas Analysis						
H_2	97.444	98.268	99.698	96.039	99.890	99.566
C_3H_8	0.010	0.004		0.006	0.003	0.004
C_3H_6						
H_2S	1.669	1.197	0.169	2.425	0.025	0.258
i-C_4H_{10}	0.050			0.053		
n-C_4H_{10}	0.774	0.344	0.021	0.949	0.024	0.073
1-C_4H_8		0.062		0.112	0.019	0.033
i-C_4H_8		0.001	0.013			
t-C_4H_8		0.033	0.011	0.229	0.007	0.017
c-C_3H_8		0.065		0.160	0.005	0.016
C_2H_6						
N_2	0.054	0.026	0.024	0.027	0.026	0.032
CH_4						
Liquid Analysis (wt % of feed)						
Thiophene	0.02	5.10	9.81	0.70	6.34	8.25
Cyclohexane	36.91	30.70	32.44	38.38	17.05	29.76
Cyclohexene	0.11	12.63	15.04	8.95	8.81	13.76
Isoctene	0.00	1.54	11.17	0.38	6.60	9.03
Toluene	29.27	31.81	36.35	36.09	20.52	33.71
Napthalene	1.31	7.70	8.98	7.95	3.82	9.78
Quinoline	0.41	0.23	0.03	0.92	0.03	0.43
Conversion (wt %)						
Thiophene	99.80	48.90	2.90	93.10	37.30	18.40
Cyclohexane	-42.10	-18.20	-25.40	-48.30	34.10	-15.10
Cyclohexene	99.20	5.40	-12.40	33.10	34.20	-2.80
Isoctene	100.00	84.50	-11.70	96.20	34.00	9.70
Toluene	2.20	-6.30	-21.50	-20.60	31.50	-12.60
Naphthalene	81.30	-10.40	-27.40	-12.80	45.80	-38.70
Quinoline	89.00	93.70	99.20	75.20	99.30	88.50

TABLE 21. Deactivated F145 Catalyst

Exp No.	F145DA	F145DB	F145DC	F145DD	F145DE	F145DF
Impregnation Conditions	Deactivated F145 catalyst supplied by CANMET					
Hydrotreating						
Temp (°C)	350	300	250	350	250	300
Press (MPa)	5.2	3.4	5.2	1.7	1.7	3.4
Yield Summary						
Liquid (wt % feed)	84.0	96.4	94.9	93.4	95.8	94.9
Gas (wt % feed)	4.2	1.1	0.4	2.7	0.2	1.0
H_2 Consumption	0.0047	-0.0016	-0.0022	-0.0011	-0.0026	-0.0013
Sulphur Conv %	59.2	11.1	1.5	26.1	0.1	7.7
Gas Analysis						
H_2	97.482	99.436	99.771	98.618	99.896	99.461
C_2H_6	0.005	0.002		0.004		
C_3H_6				0.001		
H_2S	1.718	0.284	0.038	0.695	0.003	0.198
i-C_4H_{10}	0.085	0.022		0.040		
n-C_4H_{10}	0.575	0.061	0.013	0.132	0.001	0.041
1-C_4H_8	0.019	0.038	0.015	0.103	0.008	0.044
i-C_4H_8				0.048		
t-C_4H_8	0.044	0.059	0.009	0.172	0.001	0.048
c-C_3H_8	0.028	0.041	0.008	0.125		0.036
C_2H_6						
N_2	0.044	0.058	0.148	0.061	0.090	0.172
CH_4						
Liquid Analysis (wt % of feed)						
Thiophene	0.41	8.93	9.62	7.89	9.14	7.91
Cyclohexane	32.75	30.40	27.29	31.35	24.29	24.85
Cyclohexene	1.05	13.85	12.68	13.04	13.11	11.12
Isoctene	0.12	7.39	9.99	6.02	9.39	7.22
Toluene	27.18	33.07	30.84	35.00	28.74	28.00
Napthalene	6.01	7.87	7.55	8.51	7.07	6.83
Quinoline	0.45	0.06	0.00	0.26	0.03	0.05
Conversion (wt %)						
Thiophene	95.90	10.60	3.60	20.90	8.40	20.70
Cyclohexane	-26.10	-17.10	-5.10	-20.70	6.50	4.30
Cyclohexene	92.10	-3.80	5.00	2.30	1.80	16.70
Isoctene	98.80	26.00	-0.00	39.70	6.00	27.70
Toluene	9.20	-10.50	-3.00	-16.90	4.00	6.50
Naphthalene	14.70	-11.60	-7.10	-20.70	-0.30	3.10
Quinoline	87.90	98.50	100.00	93.00	99.20	98.70